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Short Communication

EXTRACTIVE-SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) AS AN ION-ASSOCIATION COMPLEX WITH 4-(2-PYRIDYLAZO)-RESORCINOL AND TETRABUTYLAMMONIUM PERCHLORATE

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Abstract

A simple and sensitive extractive- spectrophotometric method for the determination of trace amounts of vanadium(V) is reported. The method is based on the quantitative extraction of the anion complex of V(V) with 4-(2-pyridylazo)-resorcinol with tetrabutylammonium perchlorate into chloroform, followed by spectrophotometric measurements at 554 nm. Beer's law is obeyed over the concentration range of 5-350ng ml^{-1} at 554 nm with a molar absorptivity of $1.3 \times 10^5 l\ mol^{-1}\ cm^{-1}$. The relative standard deviation is 1.6% for a 100 ng ml^{-1} vanadium solution. The interfering effect of various cations and anions was studied. The method was applied to the determination of vanadium is some synthetic samples.

Introduction

The analytical chemistry of vanadium has developed considerably in recent years owing to its important industrial and biological uses. The most important use of vanadium is as an alloying element in the steel industry, where it is added to produce gain refinement and hardenability in steels. The principle application of vanadium in nonferrous alloys is the titanium 6-4 alloy which is becoming important in supersonic aircraft [1]. There are also several biological systems, including plants and aminals which contain significant levels of vanadium containing compounds [2-4].

Solvent extraction is a well known method of separation based on the transfer of a solute from one solvent into another, especially immiscible solvents, when they are brought in contact [5-8]. The reason for the widespread use of solvent extraction lies in the speed, ease and convenience of the technique. A survey of literature reveals that, in recent years, a variety of reagents has been utilized for the extraction spectrophotometric determination of vanadium

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[9-14] but many of them suffer from interference from metal ions such as Cr(III), Mn(VII), Pt(IV), Fe(III), Al(III), Ti (IV), Zr (IV), Mo (VI), W (VI), Hg (II), Cu (II), Ni (II), Co (II), Cd (II) and Ag (I).

In recent years, we have been involved in the development of new extraction spectrophotometric methods for a variety of biologically or environmentally important metal ions such as Os (IV) [15], K^+[16], Pd^{2+}[17], Cu^{2+}[18,19], NH_4^+ [20], Ag^+ [21], Pb^{2+} [22] and Hg^{2+} [23]. In this paper, we report a new simple, sensitive and selective method for the determination of ultra trace amounts of vanadium(V) based on the quantitative extraction of the anion complex of V(V) with 4-(2-pyridylazo)-resorcinol (PAR) with tetrabutylammonium perchlorate (TBAP) into chloroform, followed by spectrophotometric measurements at 554 nm.

Experimental Section

Reagents

All of the chemicals used were of the highest purity available and used without further purification except for vacuum drying over P_2O_5. Triply distilled deionized water was used throughout the process.

A 1000 μml^{-1} solution of ammonium meta vanadate was prepared by dissolving 0.2296 g of extra pure NH_4VO_3 (Merck) in water and diluting it to the mark in a calibrated 1000 ml volumetric flask. Working solutions were prepared by appropriate dilution of the stock solution with water.

A 2.4×10^{-4} M solution of PAR was prepared by dissolving 0.06125 g of monosodium salt of PAR (Merck) in 0.01 M lithium hydroxide and diluting to the mark in a calibrated 100 ml volumetric flask.

A TBAP solution (0.6% w/v) was prepared by dissolving an appropriate amount of the salt in pure chloroform (both from Merck). A buffer solution of pH 5.0 was prepared from 0.01 M lithium hydroxide and phosphoric acid.

Apparatus

The absorption spectra were recorded on a Beckman Model 34 ratio recording spectrophotometer and the absorbance measurements were made with a CECIL Model CE292 spectrophotometer. The pH measurements were made with a Metrohm Model 632 pH meter using a combined glass electrode.

Procedure

An aliquot of the sample solution containing 0.125-112.5 μg of V(V) was placed in a 25.0 ml calibrated flask. Five ml of buffer solution pH 5.0, 1 ml 3 M KCl and 2.5 ml of 2.4×10^{-5} MPAR was then added and the solution was diluted to the mark with water. The solution was then transferred into a 60 ml separatory funnel, where 5 ml 0.6% TBAP in chloroform was added and the mixture was shaken for 15 min at a rate of 500 rpm. The phases were allowed to separate and the absorption of the organic phase was measured at 554 nm against a reagent blank.

Results and Discussion

In preliminary experiments, it was found that the stable 1:1 complex of V(V) with PAR [24,25] could be readily extracted as a reddish violet ion-paired complex with tetrabutylammonium ion into chloroform phase. Thus, the quantitative extraction of the resulting ternary complex (VO_3-PAR-TBA) was optimized by changing variables such as pH, volume of buffer solution, concentrations of PAR and TEAP, ionic strength and shaking time.

The absorption spectra of the ternary complex of vanadium in chloroform solution and the corresponding reagent blank are shown in Figure 1. As seen, the complex shows a maximum absorbance at 554 nm, while the reagent blank possesses a negligible absorbance at this wavelength.

Effect of Variables

The effect of pH on the extraction of vanadium (V) was studied over the pH range 2-9 and the results are given in Figure 2. As seen, the formation of the retractable complex form of V(V) was found to start at about pH 2.5, became maximal at pH between 4.5 to 5.5 and then decreased at higher pH values. At pH 4.5-6.5, the VO_3-PAR complex

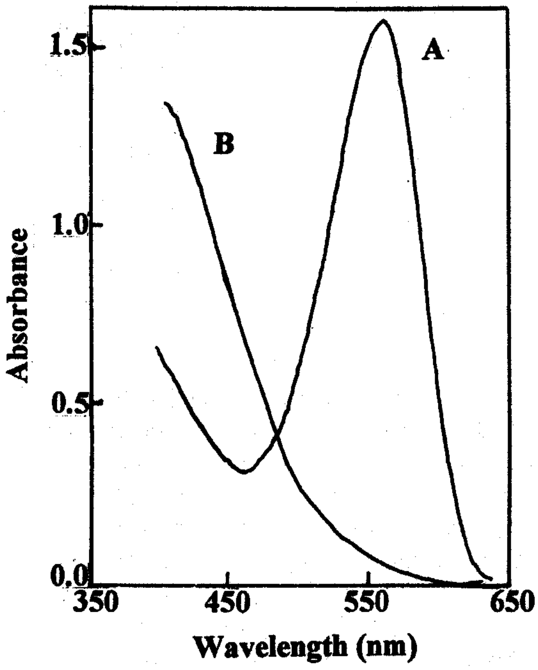

Figure 1. Absorption spectra of the ternary complex (A) and the reagent blank (B), in chloroform

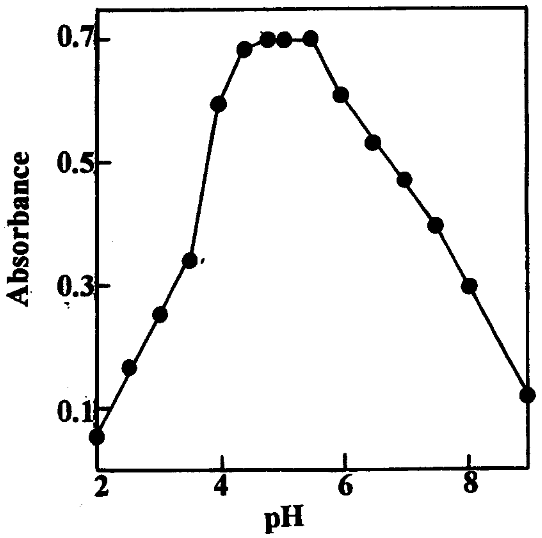

Figure 2. Effect of pH on the extraction of V(V). Conditions: V(V), 50 ng ml^{-1}; PAR, 2.4×10^{-6}M; KCl, 0.12 M; TBAP, 0.6% in chloroform

presumably exists as a univalent anionic complex, which can then be easily extracted as a neutral ternary VO_3-PAR-TBA complex into the organic phase. Hence, a pH 5.0 was chosen for all extraction purposes. The optimum volume of the buffer solution of pH 5.0 was also investigated (Fig. 3) and it was found that 5 ml of the buffer solution is necessary for quantitative extraction of V(V) into the organic phase.

The influence of PAR and TBAP concentrations on the extraction of PAR-V(V)-TBAP complex was investigated and the results are shown in Figures 4 and 5, respectively. As seen, the absorbance of the organic phase at 554 nm intensifies with an increase of both the PAR and TBAP concentrations in the aqueous and organic phase, respectively. Maximum extraction of vanadium occurs when the reagent concentration is 2.4 ×10^{-6} M PAR and 0.6% w/v TEAP in chloroform. A further excess of both reagents has no considerable effect on the measured absorbance of the organic phase, except that in the case of PAR the absorbance of the blank solution tends to increase gradually.

The change in the ionic strength of the aqueous solution, as it was adjusted by KCl solution, was found to have no considerable effect on the extraction of vanadium up to a value of about 0.9 M. The extraction of PAR-V(V)-TBAP ternary complex under the conditions recommended in the procedure is relatively rapid. A shaking time of 10-15 min at 500 rpm was found sufficient for the extraction of vanadium.

Quantitative extraction of vanadium as PAR-V(V)-TBAP complex was confirmed by observing no further enhancement in the absorbance of the mixture of two 2.5ml portions of the organic phase obtained from two successive extractions of an aqueous vanadium solution, compared with that of a 5 ml organic phase obtained from a single stage extraction of the same vanadium solution under optimal experimental conditions.

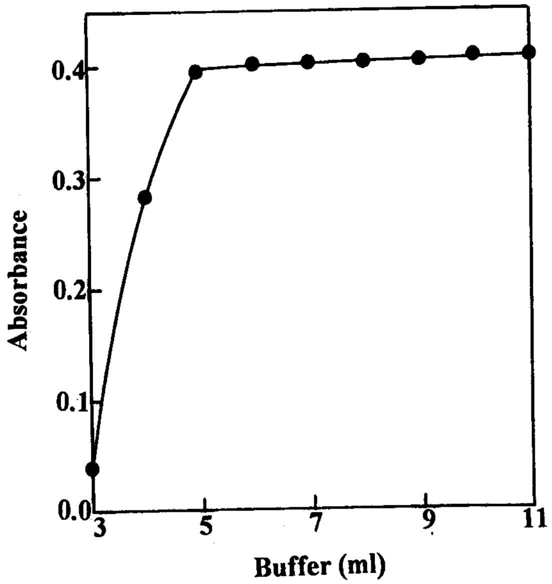

Figure 3. Effect of volume of the buffer solution of pH 5.0 on the extraction of V(V). Conditions: V(V), 50 ng ml^{-1}; PAR, 24×10^{-6} M; 0.12 M; TBAP, 0.6% in chloroform

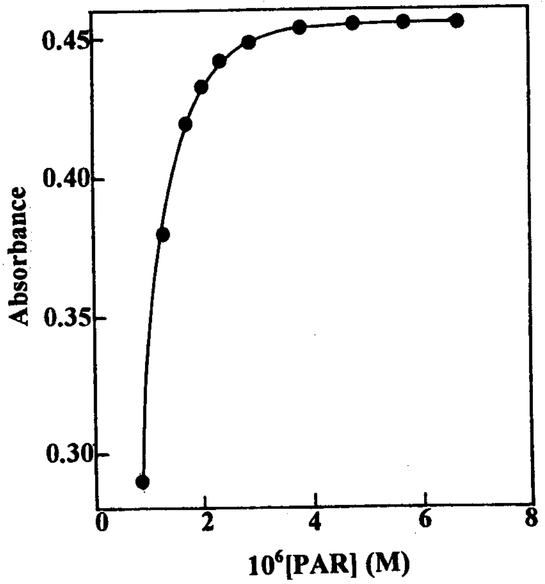

Figure 4. Effect of PAR concentration on the extraction of V(V). Conditions: V(V), 50 ng ml^{-1}; KCl, 0.12 M; pH, 5.0; TBAP, 0.6% in chloroform

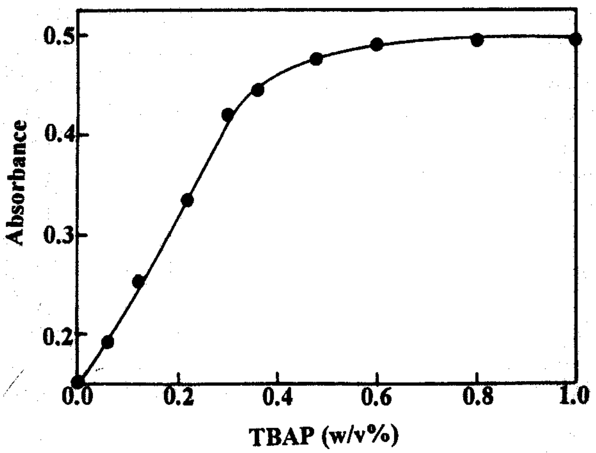

Figure 5. Effect of TBAP concentration on the extraction of V(V). Conditions: V(V), 50 ng ml^{-1}; PAR, 2.4×10^{-6}M; KCl, 0.12 M; pH, 5.0

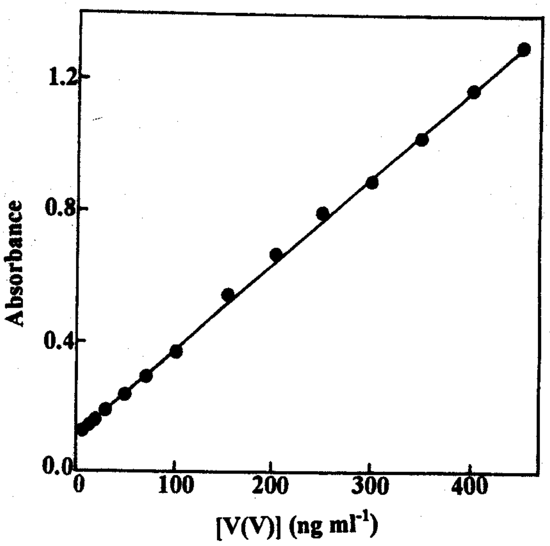

Figure 6. Calibration graph. Conditions: PAR, 2.4×10^{-6}M; KCl, 0.12 M; pH, 5.0; TBAP, 0.6% in chloroform

Calibration

Under the optimum experimental conditions described above, a linear calibration graph of absorbance vs. [vanadium] was obtained in the concentration range of 5-450 ng ml^{-1} with a regression equation $A = 0.116 + 1.3\times10^{5}$ [V] and a correlation coefficient of 0.9988 (Fig. 6). The relative standard deviation of ten replicate measurements is 1.6% for a 100 ng ml^{-1} vanadium solution.

Effect of Diverse Ions

In order to study the influence of various cations and anions on the determination of vanadium (V) ion, a fixed concentration of V(V) (100 ng ml^{-1}) was taken with different amounts of foreign ions and the recommended procedure was followed. A relative error of twice the standard deviation of measurements was considered tolerable. The results are summarized in Table 1. As seen, most of the common cations and anions associated with vanadium do not interfere in the extraction of PAR-V(V)-TBAP ternary complex.

Application

In order to assess the applicability of the proposed method to the real samples, it was applied to the determination of V(V) in four different synthetic samples and the results are shown in Table 2. It is seen that the amount of vanadium recovered from the synthetic samples containing mg/25 ml levels of different cations are in satisfactory agreement with the initial V(V) in the samples.

Conclusion

The method proposed provides a reliable means for the determination of trace amounts of vanadium. It is very

Table 1. Tolerable limits of diverese ions on the determination of 100 ng ml^{-1} vanadium

Ion	Tolerated ratio of foreign ion to V(V)
Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, F^-, Cl^-, Br^-, No_3^-	2000*
Ce^{3+}, SCN^-	1000
Al^{3+}, BrO_3^-, IO_3^-	700
Mn^{2+}, Cd^{2+}	500
Ni^{2+}, Co^{2+}	300
WO_4^-	100
MnO_4^-	50
Cu^{2+}, CN^-	5
Bi^{3+}, Fe^{3+}, Zr^{4+}, MoO_4^-	3

*Concentrations above the stated value was not tested.

Table 2. Vanadium determination in synthetic samples

No	Sample matrix*	V(V) added	V(V) found
1	Ni^{2+}(3), Co^{2+}(2), Ba^{2+}(7)	12.5	12.4
2	Mn^{2+}(4), Cd^{2+}(5), Zn^{2+}(2)	12.5	12.6
3	Ba^{2+}(8), Cd^{2+}(4), Sr^{2+}(7)	12.5	12.4
4	Al^{3+}(3), Ca^{2+}(6), Na^+(7)	12.5	12.5

*mg/25 ml of the cations are given in parantheses.

sensitive and free from interferences from many cations and anions. The method is superior in ease, sensitivity and selectivity with most published methods for the determination of vanadium by use of ion-association compounds.

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