

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH *N*-PHENYLCINNAMOHYDROXAMIC ACID AND MONOCHLOROACETIC ACID OR TRICHLOROACETIC ACID

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ABSTRACT. Vanadium(V) was found to react with *N*-phenylcinnamohydroxamic acid (PCHA) in the presence of monochloroacetic acid or trichloroacetic acid to form reddish-violet complexes of stoichiometry 1:2:1 (V:PCHA:X, where X = monochloroacetic acid or trichloroacetic acid). The complexes are quantitatively extractable into chloroform from 3-10 and 2-5 M solutions of monochloroacetic acid and trichloroacetic acid, respectively. The spectra of the complexes exhibited absorption maxima at 530 and 542 nm with molar absorptivities of 6700 and 7750 M⁻¹cm⁻¹ for the two systems, respectively. The coloured systems obeyed Beer's law in the concentration ranges of 0.5-10 and 0.4-8 µg mL⁻¹ of vanadium(V), respectively. The methods are precise with standard deviations of 0.5 and 0.6% for ten determinations of 4 µg mL⁻¹ of vanadium(V), respectively. The effects of foreign ions on the extraction and determination of vanadium(V) for the two systems have been studied and the methods have been found to highly selective for the determination of vanadium(V) by solvent extraction and spectrophotometry. The methods have been applied to the determination of vanadium in steel, blood, and water samples with reasonable precision and accuracy.

INTRODUCTION

Several reagents have been reported in the literature for the spectrophotometric determination of vanadium(V) [1-20]. Of these reagents comparatively few are well suited for the precise and reliable determination of vanadium in complex materials. Some of these reagents are highly sensitive but not selective [1, 2, 10, 15-17] and suffer from the interferences of many common ions normally associated with vanadium in alloys and complex materials. While some of the reagents are selective but not sensitive [3-9, 12, 13, 18] and hence their applications are limited.

N-Phenylbenzohydroxamic acid [21, 22] and its analogues [2, 4, 6, 22-29] are commonly used as selective reagents for the extraction-photometric determination of vanadium(V) from concentrated hydrochloric acid solutions. However, titanium(IV), zirconium(IV), molybdenum(VI), and tungsten(VI) interfere seriously. It has also been reported [30, 31] that the extraction of vanadium(V) is not quantitative because of the partial reduction of vanadium(V) to vanadium(IV) in concentrated hydrochloric acid media.

This problem could be overcome by carrying out the extraction of vanadium(V) from carboxylic acids solutions which could further improve the sensitivity of the method by reacting with the V=O group of the vanadium(V)-hydroxamic acid complex molecule [32-34]. Hence in the present investigation the extraction of vanadium(V) with *N*-phenylcinnamohydroxamic acid (PCHA) has been studied spectrophotometrically in detail in the presence of monochloroacetic acid (MCAA) and trichloroacetic acid (TCAA) to develop sensitive and selective methods for the precise and reliable determination of vanadium(V).

The present investigation has led to the development of new methods for the extraction and spectrophotometric determination of vanadium(V) with *N*-phenylcinnamohydroxamic acid and monochloroacetic acid or trichloroacetic acid. The proposed methods do not involve the use of hydrochloric acid and hence there is no danger of any reduction of vanadium(V) during its extraction. The methods have been applied successfully to the determination of vanadium in steel, blood, and water.

EXPERIMENTAL

Equipment and reagents. A Beckman model 24 UV-Visible spectrophotometer equipped with 1-cm cells was used for recording the absorption spectra and absorbance measurements.

Distilled water was used throughout. Chloroform (Aristar, AnalaR) was washed several times with water to remove the ethanol. It was distilled and dried over anhydrous calcium chloride before being used. All chemicals were of analytical reagent-grade unless otherwise stated.

A stock solution of vanadium(V) was prepared by dissolving 1.1700 g of ammonium metavanadate (BDH, AnalaR) in water, acidified with nitric acid, and diluted to 1.0 L with water. The solution was standardized conventionally. A working solution was prepared by diluting a suitable aliquot of the standard solution to a known volume with water. Solutions of foreign ions were prepared by dissolving known quantities of reagent grade salts in water to give 10 mg mL⁻¹ of the ion in question. The solutions were acidified whenever necessary to prevent the hydrolysis. In general nitrate salts were used for the cations and sodium or ammonium salts were used for the anions.

N-Phenylcinnamohydroxamic acid, PCHA, was prepared by the reported method [22]. A 0.005 M solution of the reagent, PCHA, in ethanol-free chloroform was used for the extraction. Stock solutions of monochloroacetic acid (10 M) and trichloroacetic acid (5 M) were prepared by dissolving the respective acids in water.

Preparations of sample solutions

Steel. A weighed quantity of the steel sample (0.1 g) was heated gently in a 400-mL beaker with 10 mL of concentrated nitric acid until the brisk reaction ceased, 5-10 mL of aqua-regia was added and the solution was evaporated to near dryness to expel nitrogen oxides. The residue was dissolved in 50-mL of slightly acidified (hydrochloric acid) water by heating. The undissolved silicic acid and hydrated tungstic acid were filtered off and washed several times with water. The filtrate and washings were transferred to a 100-mL volumetric flask and diluted to volume with water. Suitable aliquots of this solution were taken for the analysis. Sodium fluoride (0.2 g) was added to the sample solution before the extraction and determination of vanadium(V).

Blood. A measured amount of the blood sample (5 mL) was transferred to a Kjeldahl flask and an aliquot of the standard solution containing 0.10 mg of vanadium was added to it. The sample

was heated with a mixture of 10 mL of concentrated nitric, sulphuric, and perchloric acids in the ratio of 3:1:1 (v/v) and evaporated to almost dryness. The residue was dissolved in 25 mL of slightly acidified (hydrochloric acid) water by heating. The solution was transferred quantitatively into a 50 mL volumetric flask and diluted to volume with water. Suitable aliquots of this solution were taken for the analysis. Sodium fluoride (0.2 g) was added to the sample solution before the extraction and determination of vanadium(V).

Water. An aliquot of the standard solution containing 1.00 mg of vanadium was added to 100 mL of tap water. Suitable aliquots of this solution were taken for the analysis.

General procedure. An aliquot of the solution containing up to 200 μg of vanadium(V) was transferred into a 60-mL separatory funnel. The acidity of the solution was adjusted to 5-6 M and 2-3 M with monochloroacetic acid or trichloroacetic acid, and the volume of the aqueous phase to 10 mL with water. A 10 mL aliquot of 0.005 M PCHA solution in chloroform was added to the funnel and the mixture was shaken vigorously for 3-4 min. The funnel was allowed to stand to separate the two phases. The organic phase was collected in a 50-mL beaker containing about 2 g of anhydrous sodium sulphate. The coloured extract was transferred to a 25-mL volumetric flask and the beaker was washed with a few mL of chloroform. The washings were added to the flask and the solution was diluted to volume with chloroform. The absorbance of the coloured extract was measured at 530 or 542 nm against chloroform for monochloroacetic acid or trichloroacetic acid system, respectively.

For calibration, 0.25, 0.50, 1.00, 1.50, and 2.00 mL of a standard solution containing 100 μg mL^{-1} vanadium(V) were used with the above procedure.

RESULTS AND DISCUSSION

Acidity and absorption spectra. The extraction of vanadium(V) with PCHA in water immiscible organic solvents was examined from aqueous acetic acid, monochloroacetic acid, and trichloroacetic acid media. It was found that the extraction of vanadium(V) was incomplete from up to 10 M acetic acid solutions and at higher concentrations of the acid there was no phase separation. Furthermore the complex exhibited different absorption spectra at different concentrations of the acid and it was not stable.

Vanadium(V) was found to be quantitatively extractable with PCHA in water immiscible organic solvents from aqueous monochloroacetic acid and trichloroacetic acid media. The optimum concentration ranges of monochloroacetic acid (MCAA) and trichloroacetic acid (TCAA) in the aqueous phase for the complete extraction of vanadium(V) were found to be 3-10 and 2-5 M, respectively. At lower concentrations of the acids the formation of the mixed ligand complexes were incomplete. While at higher concentrations of acids, phase separation was difficult in both the systems due to increasing miscibility of the organic and aqueous phases. The spectra of V(V)-PCHA complexes extracted from monochloroacetic acid and trichloroacetic acid exhibited broad absorption bands at 530 and 542 nm with molar absorptivities of 6700 and 7750 $\text{M}^{-1} \text{cm}^{-1}$, respectively.

It should be noted that the spectrum of V(V)-PCHA complex extracted from hydrochloric acid [22, 23] exhibits absorption band at 540 nm with molar absorptivity of 6300 $\text{M}^{-1} \text{cm}^{-1}$. Thus the extraction of vanadium(V) with PCHA from monochloroacetic acid and trichloroacetic acid has resulted in higher sensitivity of the colour reaction.

The absorption spectrum of the reagent (PCHA) showed negligible absorption in the region

700-500 nm, slightly increasing absorption between 500-400 nm, and strong absorption beyond 400 nm. Hence, a reagent blank is not necessary for the measurements of absorbance at wavelengths >500 nm.

Several organic solvents such as chloroform, carbon tetrachloride, benzene, toluene, chlorobenzene, 1,2-dichlorobenzene, and xylene were found to extract both the complexes from the aqueous phase. The absorption spectra of the individual complex were found to be similar in all the non-polar organic solvents. However, slight variations in absorbance values were noticed. Chloroform was found to be the most suitable solvent for extraction of both the V(V)-PCHA-MCAA and V(V)-PCHA-TCAA complexes because the quantitative extraction of both the complexes was readily accomplished in it and because of the higher sensitivity of the colour reactions than in other solvents. It was also preferred because of relatively higher solubility of PCHA in it than in other solvents.

Composition of the complexes. The composition of V(V)-PCHA-X complexes (where X = MCAA or TCAA) were determined by different spectrophotometric methods [35]. The mole ratio and continuous variation methods were used to determine the ratio of vanadium(V) to PCHA while the extraction method was used to determine the ratio of vanadium(V) to monochloroacetic acid or trichloroacetic acid. The results obtained by both the mole ratio and continuous variation methods indicated that the ratio of vanadium(V) to PCHA to be 1:2 in both the complexes. The results of the extraction method indicated the ratio of vanadium(V) to MCAA or TCAA to be 1:1 in the mixed ligand complexes. Thus the overall composition of vanadium(V)-PCHA-X mixed ligand complex was found to be 1:2:1 (V: PCHA:X).

Effect of experimental variables. The effect of experimental variables on the extraction and determination of vanadium(V) was studied by taking 100 μg of vanadium(V) and determining the vanadium(V) content of the solutions by the general procedure described above.

An 8-fold molar excess of the reagent, PCHA, was found to be necessary for the complete extraction of vanadium(V) from the aqueous phase in the presence of monochloroacetic acid or trichloroacetic acid under optimum experimental conditions. A large excess of the reagent up to 50-fold molar excess had no adverse effect on the extraction of vanadium(V) from the aqueous phase in both the systems. It has also been found that there were no shift in the wavelengths of maximum absorption with varying amount of reagent.

The wavelengths of maximum absorption and absorbance values of coloured extracts of both the complexes were not affected by changes in ionic strength of the aqueous phase between 0.5 and 1.5 M with respect to potassium chloride or potassium nitrate. Variation in the temperature of both the systems between 10 and 40 $^{\circ}\text{C}$ did not produce any significant change in the absorbance values of the coloured extracts of both the systems. It was also found that the volume of the aqueous phase can be varied from 5 to 25 mL with respect to a fixed volume of 10 mL of the organic phase without any significant variation in the absorbance values or extraction efficiency of both the complexes. Further increase in volume of the aqueous phase resulted in incomplete extraction of vanadium(V) due to increasing miscibility of the two phases.

The V(V)-PCHA-MCAA and V(V)-PCHA-TCAA complexes were completely extracted into chloroform within 4 min. The chloroform extracts of both the V(V)-PCHA-MCAA and V(V)-PCHA-TCAA complexes were stable for at least 3 days at 20 ± 2 $^{\circ}\text{C}$.

Photometric characteristics of the complexes. The photometric characteristics of the coloured systems are summarized in Table 1. These results clearly indicate that the proposed methods are sensitive and precise and hence applicable to the determination of traces of vanadium.

Effect of foreign ions. In order to evaluate the selectivity of the newly developed methods, the effects of foreign ions on the extraction and determination of vanadium(V) with PCHA in the presence of monochloroacetic acid and trichloroacetic acid were studied by adding known

Table 1. Photometric characteristics of the coloured systems.

Parameter	V(V)-PCHA-MCAA system	V(V)-PCHA-TCAA system
λ_{\max} , nm	530	542
ϵ_{\max} , $M^{-1} \text{ cm}^{-1}$	6700	7750
Sensitivity [36], $\mu\text{g V cm}^{-2}$	0.0076	0.0066
Detection limit [37], $\mu\text{g mL}^{-1} \text{ V}$	0.053	0.046
Concentration range from Beer's law, $\mu\text{g mL}^{-1} \text{ V}$	0.5-10	0.4-8
Relative standard deviation ($4 \mu\text{g mL}^{-1} \text{ V}$, $n = 10$), %	0.5	0.6

Table 2. Tolerance limits of foreign ions in the determination of 100 μg of vanadium(V).

Ion	V(V)-PCHA-MCAA	V(V)-PCHA-TCAA
	Tolerance limit, mg	Tolerance limit, mg
Fluoride	95	95
Li^+ , Na^+ , K^+ , NH_4^+ , acetate, chloride, nitrate, sulphate	50	50
Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , citrate, tartrate, borate	20	20
Al^{3+} , As^{5+} , Sb^{3+} , Bi^{3+} , Sn^{4+} , Pb^{2+} , Tl^+ , La^{3+} , Th^{4+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Cr^{3+} , Mn^{2+} , PO_4^{3-} , oxalate, EDTA	10	10
Zr^{4+}	9	9.5
Fe^{3+}	7.5*	7.5*
Ce^{4+}	4	5
UO_2^{2+}	2	2.5
WO_4^{2-}	2	2
Ti^{4+}	1.5*	2*
MoO_4^{2-}	1	1

* Masked with fluoride.

quantities of the ion to a solution containing 100 μg of vanadium(V) and determining the vanadium(V) by the procedure described above. The tolerance limits of foreign ions, taken as amount (mg) which cause an error less than 2%, are given in Table 2.

Iron(III) and titanium(IV) react with the reagent to form red and yellow coloured complexes extractable into chloroform and therefore interfere in the determination of vanadium(V) by both the V(V)-PCHA-MCAA and V(V)-PCHA-TCAA systems. The interferences of both iron(III) and titanium(IV) were eliminated by masking the two ions with fluoride before the extraction of vanadium(V).

The results given in Table 2 clearly indicate that almost all common ions which are normally associated with vanadium(V) in ores, alloys, steels, and complex materials do not interfere in the

determination of vanadium(V) with PCHA in the presence of monochloroacetic acid and trichloroacetic acid. Hence the newly developed methods are selective and can be applied for the determination of vanadium(V) in diverse samples.

Applications of the methods. The newly developed methods were applied to the determination of vanadium in British Chemical Standard (BCS) steel, human blood, and potable water to assess their analytical potentiality. The vanadium content of steel samples was determined by the proposed methods. The results are given in Table 3. The blood sample from a normal adult man and the potable water did not contain any detectable amount of vanadium. Hence, known amounts of vanadium were added to the blood sample before its decomposition and to the water sample. The vanadium content of the sample solutions were determined by the proposed methods. The results are given in Table 4. The results of the analyses indicate that the newly developed methods are precise and reliable for the determination of vanadium in diverse samples.

Table 3. Determination of vanadium in BCS steel

BCS steel No.	Vanadium certified (%)	V(V)-PCHA-MCAA method	V(V)-PCHA-TCAA method
		Vanadium found* (%)	Vanadium found* (%)
64a	1.57	1.54 ± 0.03	1.55 ± 0.02
64b	1.99	1.95 ± 0.05	1.96 ± 0.04
241/1	1.57	1.53 ± 0.04	1.54 ± 0.03

*Mean ± 95% confidence limit of five determinations.

Table 4. Determination of vanadium in human blood and potable water

Sample	Vanadium added $\mu\text{g mL}^{-1}$	V(V)-PCHA-MCAA method	V(V)-PCHA-TCAA method
		Vanadium found* $\mu\text{g mL}^{-1}$	Vanadium found* $\mu\text{g mL}^{-1}$
Blood	20.00	19.84 ± 0.31	19.90 ± 0.22
Water	10.00	9.92 ± 0.15	9.95 ± 0.13

*Mean ± 95% confidence limit of five determinations.

CONCLUSION

Two new methods for the extraction and spectrophotometric determination of vanadium(V) with *N*-phenylcinnamohydroxamic acid and monochloroacetic acid or trichloroacetic acid have been developed. The methods are sensitive, selective, and free from the rigid control of experimental variables. The methods are precise and reliable and compare favourably with the methods

reported in literature for the determination of vanadium in terms of both the sensitivity [3, 4, 6, 7, 18, 21-25, 27-29] and the selectivity [2, 4, 7, 11, 15-20]. The methods can be applied for the determination of vanadium in diverse samples.

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