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

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TO MY FATHER, ATO ABEBAW MENGSTIE

AND MY MOTHER W/o BIZUNESH AYANE

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ABSTRACT

Solvent Extraction and Spectrophotometric Determination of Vanadium (V) with N-Phenylcinnamohydroxamic Acid and Azide or Trichloroacetic Acid

by

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N-phenylcinnamohydroxamic acid, PCHA, was found to react with vanadium (V) in the presence of azide or trichloroacetic acid (or chloroacetic acid) to form water insoluble bluish-violet and reddish-violet complexes, respectively. The vanadium (V)-PCHA-N_3 complex was quantitatively extractable into chloroform and other organic solvents at 0.03-1.5 M acidity with respect to HCl. While the vanadium (V)-PCHA-TCAA was quantitatively extractable at 2-5 M acidity with respect to trichloroacetic acid, TCAA. The vanadium (V)-PCHA-N_3 and vanadium (V)-PCHA-TCAA complexes have absorption maxima in the visible region at 560 and 542 nm with molar absorptivity of 6300 and 7750 l $mole^{-1}$ cm^{-1}, respectively. The colored systems obeyed Beer's law in the concentration range of 0.9-10 ppm of vanadium in the presence of azide and 0.60-8.0 ppm of vanadium in the presence of trichloroacetic acid. The composition of the complexes have been determined and found to be 1:2:1 (V:PCHA:N_3)

and 1:2:1 (V:PCHA:TCAA). The effect of foreign ions and other experimental variables on the extraction and determination of vanadium (V) have been studied in both systems. On the basis of these studies two simple, precise, sensitive and highly selective methods ahve been developed for determination of vanadium (V) by solvent extraction and spectrophotometry. The two newly developed methods ahve been applied for the successful determination of vanadium in steel and blood samples.

I. INTRODUCTION

Vanadium has an abundance in nature of about 0.02% (1). It is widely spread but there are few concentrated deposits. Its important mineral sources are patronite (a complex sulfide), vanadinite [$Pb_5(VO_4)_3Cl$], and carnotite [$K(UO_2)VO_4.3/2H_2O$]. Very pure vanadium is rare, because, it is quite reactive towards oxygen, nitrogen, and carbon at the elevated temperature used in conventional thermometallurgical processes. Since its chief commercial use is in alloy steels and cast iron, to which it lends ductility and shock resistance, commercial production is mainly as an iron alloy, ferrovanadium (2). It is also used as a catalyst both in nature and in industries.

Vanadium has been shown to replace molybdenum in the nitrogen-fixing function of Azotobacter chrococcum but not of other species (3). The algae scendesmus exhibits improved photosynthesis in the presence of vanadium, which may thus be beneficial or required for the process (4). The role of vanadium in normal animal metabolism is not completely understood. Rather extensive literature exists on the toxicology of compounds of this metal and its distribution in plants and animals (4). It is ubiquitous, but there is no conclusive evidence available which suggests that vanadium is essential in normal metabolic processes in animals.

I.1 Analytical Chemistry of Vanadium

The oxidation state of vanadium in compounds varies from -1 to +5. In some reactions vanadium is similar to the other elements

(niobium, tantalum) of Group VB; sometimes also to molybdenum and tungsten of Group VIB.

In aqueous solution vanadium most frequently occurs as the colourless vanadate (V) ion which forms yellow poly acids in strongly acidic medium. Vanadate can be reduced consecutively to the blue V(IV) or [VO(II)] compounds, the green vanadium (III) salts, and finally to the violet vanadium (II) salts.

Quinquevalent and quadrivalent vanadium have a predominant affinity for oxygen as donor atoms. In complex compounds vanadium (V) has co-ordination number six and probably forms octahedral species. Vanadium (IV) complex has a square pyramid configuration, which is transformed to an octahedron through co-ordination of a further ligand. Vanadium (III) has often a co-ordination number of six in complexes which may be formed with ligands containing O, N or S as donor atoms. Bivalent vanadium is usually hexa co-ordinate, forming octahedral complexes with oxygen or nitrogen containing ligands. The complexes of vanadium in the other oxidation states are rare and have not found application in analytical chemistry (1,5).

Detection and Separation of Vanadium (6): The red-brown color produced when an acid solution of vanadium (V) is treated with hydrogen peroxide is thought to be due to the formation of a compound of the type O_2VX_3 or possibly $[O_2VX_5]^{=}$. A large excess of hydrogen peroxide changes the color of the solution from red-brown to yellow and reduces the color intensity, supposedly by a shift in the equillibrium.

$$\underset{\text{red-brown}}{(VO_2)_2(SO_4)_3} + 6H_2O \xrightarrow[H_2SO_4]{H_2O_2} \underset{\text{yellow}}{2VO_2(OH)_3} + 3H_2SO_4 \qquad [1]$$

Even though other metals like titanium and molybdenum (VI) give colors with hydrogen peroxide, the above color reaction is mostly employed for the detection of vanadium. This is because the titanium color can be bleached by fluoride, which in moderate amounts does not affect the vanadium color. Because of its fairly strong oxidizing power in acid medium, vanadium (V) transforms various organic compounds into colored products which can be made to serve as the basis for qualitative tests and determination of vanadium (V) by indirect methods. Among reagents in this category are diphenylamine and diphenylamine sulfonic acid (blue color), 3, 3'-dimethylnaphthidine (red-violet color), benzidine (yellow color) and strychnine (violet color passing into orange). The interference of ferric ion can usually be prevented by addition of phosphoric acid.

Vanadium can be separated from other metals by different methods which includes, precipitation methods, extraction methods, paper chromatographic separation and by use of anion-exchange resin. A useful way of separating vanadium from iron, titanium, etc., is by fusing the sample with sodium carbonate (together with a little potassium nitrate if necessary) or sodium peroxide and leaching the melt with water. Ammonia precipitation in the presence of ferric iron serves to separate vanadium (V) at high dilutions. Ten mg. of iron in a liter is sufficient for complete precipitation of as much as 30 µg. vanadium. The final pH of the solution should

be 6-7. Elements such as chromium (III) molybdenum (VI), titanium (IV) and tin coprecipitate.

Vanadium (V) cupferrate, like most other cupferrates, is soluble in chloroform and other brganic solvents. Since vanadium cupferrate can be quantitatively precipitated in a dilute mineral acid medium, it may be inferred that it can be extracted by chloroform from the same medium. Vanadium (V) can be extracted from a weakly acidic solution (optimum pH 3.5-4.5) with a chloroform solution of 8-hydroxy quinoline. This separation was first applied as a means of isolating, vanadium from the fiiltered leach of sodium carbonate melt and separating it from chromium (VI). After evaporation of the chloroform, the residue can be fused with sodium carbonate and vanadium transformed into vanadate. A considerable number of metals are extracted in weakly acidic solution, notably iron (III), molybdenum (VI), copper, and, partly, aluminum.

Methods for Determination of Vanadium: It has been reported that vanadium can be determined by gravimetric (8,9), Volumetric (9,10), and atomic absorption spectroscopic methods. The element as vanadate can be determined gravimetrically precipitating it as Ag_3VO_4 and drying the precipitate at 110°C. It has been stated that the results obtained by precipitation of vanadate as Ag_3VO_4 are not altogether satisfactory. Better results are obtained by precipitation at pH 4.5 as $AgVO_3$, the precipitate being weighed after drying at 100-105°C.

The volumetric determination of vanadium as vanadates can be performed by using iodides in strongly acid (hydorchloric) solution in an atmosphere of carbondioxide to reduce the vanadate (V) to the quadrivalent condition. The liberated iodine and the excees of iodine is determined by titration with standard potassium iodate solution. Both the gravimetric and volumetric methods for the determination of vanadium are not sensitive (concentrations less than 10^{-3} M are not determined) and selective since several metal ions interfere in the determination.

The use of atomic absorption spectroscopy for the determination of vanadium also suffers from lack of sensitivity and selectivity. Using the most sensitive resonance line, 318.4 nm, the minimum concentration that can be detected is 1000 ppm, using air-acetylene flame and, 2 ppm using nitrous oxide- acetylene flame. Several metal ions like Li^{+}, Na^{+}, K^{+}, Cs^{+}, Fe^{3+}, Cr^{3+}, Bi^{3+}, Al^{3+}, etc. interfere. Wendt and Fassel (11) reported a sensitivity of 3 ppm with the above resonance line, using an induction coupled plasma. Solvent extraction-spectrophotometric methods, which are found to be more selective and sensitive, are used for the determination of vanadium. Extraction spectrophotometric methods are based on chemical reactions of the metal ion usually with suitable organic reagents.

The organic reagents confers many advantages over inorganic reagents for extractive-spectrophotometric determination of metal ions. The detections and determinations of substances with organic reagents can often be performed with higher sensitivity

and selectivity. The separations are also more effective when organic reagents are employed. A large number of organic reagents are known and thus, a better choice can be made. It is also possible to synthesize a new reagent possessing more advantageous properties for a given analytical problem. The study of these reagents still allow the development of highly sensitive, selective, and rapid methods for the analysis of a variety of materials needing only simple instrumentation. Therefore, the scope and number of their applications in analytical practice continues to increase.

The reactions of organic reagents with inorganic ions in solution can yield products of various properties. The reaction products may be complex compounds, or new organic substances (formed due to oxidation-reduction or catalytic action of inorganic ions) or other forms of the reagent (acid-base indicators). Besides these reaction types the organic reagent in solution can be absorbed on a precipitate of an inorganic substance, the absorption being accompanied by a color change of the reagent (absorption indicators). The formation of a product which is insoluble in a given solvent (usually water) can be employed in the gravimetric determination, separation or precipitation titration of an ion. If the reaction product is volatile, the organic reagent can be used for analytical separation based on distillation or sublimation. Organic reagents can also be used for masking the interferring ions based on the formation of stable and soluble complexes.

In many reactions of organic reagents a conspicuous color or fluorescence is developed, or conversely, a colored component in solution is decolorized during the reaction, or its fluorescence is quenched. Such reactions can be applied both for qualitative tests and for spectrophotometric or fluorimetric determinations. If the reaction product is less soluble in water than in an organic solvent immiscible with water, the reaction can be used for the solvent extraction of any of its parent constituents. Of the several types of reactions of organic reagents with inorganic ions those producing coloured products and well suited for solvent extraction are widely used for the photometric determination of the metal ions (5, 12-16). The present investigation is also based on solvent extraction and spectrophotometry hence, a brief review of these techniques is given in the following sections.

1.2 Spectrophotometric Determination of Metal Ions:

Spectrophotometry is based on the measurements of the absorbance for monochromatic light passing through the solution containing the substance to be determined. The sensitivity, selectivity and reliability of the method heavily depends on the nature of the organic reagent used.

Sensitivity and selectivity: Sensitivity is one of the obvious demands in applications of analytical methods. In order to comply with this requirement for reactions which involve a change in color, the molecule of the complex formed or the organic reagent itself must contain chromophoric groups which are charac-

terized by transitions with molar absorption coefficients in the range $10^3 - 10^5$ l $mole^{-1}$ cm^{-1}. Such chromophoric groups are found among d-π and π chromophores. The complexes with d-π chromophores are restricted to the analysis of transition metal ions, in particular those which can exist in two oxidation states differing by one electron. The reagents with π-electron groups are useful to the analysis of most metal ions. The main reason can be found in the intensity of the transitions (with molar absorption coefficients up to 10^5 l $mole^{-1}$ cm^{-1}) which characterize these chromophoric groups. By introducing suitable substitutents into the molecules of the organic reagents one can increase the sensitivity and selectivity of spectrophctometric determinations.

If adequate selectivity in spectrophotometric determination of a given substance is to be achieved, some practical considerations must also be taken into account. For example, it is necessary to choose a suitable wavelength at which to make the measurement. The absorption coefficient of the substance being determined should be high, and those of other substances present be negligable. Selectivity can also be increased by the proper adjustment of pH or by masking. Of course the masking reagent (and the complexes formed) should be colorless and not form any complexes with the metal being determined or react with the colorimetric reagent. The selectivity of the spectrophotometric determinations can further be increased by solvent extraction of the reaction product.

Accuracy and Precision: Both the accuracy and precision of a photometric determination depend on the completness of a given reaction: $M+nL \rightleftharpoons ML_n$. As the reaction solution usually contains components competing in the reaction (buffering and masking agents), it is necessary to consider the conditional constant for the general complexation equilibrium on which the determination is based. The ligand is usually an anionic species of a weak acid and so its concentration is pH-dependent.

If a reaction is considered as complete when 99% of the metal being determined is transformed into the particular complex ML_n, it holds that

$$\frac{[ML_n]}{C'_M} = \beta'_{ML_n} (C'_L)^n \geq 10^2. \qquad [2]$$

where C'_M is the total concentration of the metal unconsumed, C'_L is the total concentration of the ligand unconsumed in the formation of the complex ML_n and β'_{ML_n} is the conditional constant for general complexation equilibrium. The expression in equation 2 can be used for the calculation of the necessary minimum excess of the reagent, or for estimation of the pH range over which β'_{ML_n} attains the required value, provided that the concentration of the buffer, the dissociation constants of the reagent, and the stability constants of the particular complexes are known.

In determination of metal, M, in presence of another metal, N, if both form colored complexes, ML_n, and, NL_n, with similar

absorption spectra, correct results for ML_n are obtained if the following condition is fulfilled:

$$\frac{[ML_n]}{C'_m} = \beta'_{ML_n} (C_L)^n \geq 10^2 \qquad [3]$$

at the same time the following expression must hold for the ratio of the absorbance values of the two complexes, provided that the colorimetric reagent itself does not absorb at the wave length used:

$$\frac{A_{ML_n}}{A_{NL_n}} = \frac{\varepsilon_{ML_n}[ML_n]}{\varepsilon_{NL_n}[NL_n]} \geq 10^2 \qquad [4]$$

If the concentrations of M and N are the same and the absorption coefficients of the two complexes are equal, the concentration of the complex NL_n must be negligible if an accurate result is to be obtained for , M:

$$\frac{[NL_n]}{C'_n} = \beta'_{NL_n} (C'L)^n \leq 10^{-2} \qquad [5]$$

or

$$\frac{\beta'_{ML_n}}{\beta'_{NL_n}} \geq 10^4 \qquad [6]$$

The values of the conditional stability constants depend on the pH of the solution as well as on the presence of all competing components.

1.3 Spectrophotometric Methods for the Determination of the Composition of Complexes

The optical properties of solutions containing complexes usually differ from those of the constituent ions or molecules.

The change in the optical behaviour is closely related to the formation of co-ordinate bonds. Analytical methods based on the measurements of light absorption can be used to advantage for studying complexation equilibria, since they are suited to the selective determination of very small concentrations of certain species without changing the composition of the solution. The determination can usually be rendered selective by an appropriate choice of the wavelength. The basic condition for application of all analytical methods based on the measurement of light absorption is that the Beer-Lambert law is obeyed by the constituents to be determined. In the present investigation, the mole ratio method (17), the continuous variations method (18), and the simple spectrophotometric method (19) have been employed for the determination of the composition of the complexes. Hence, a brief review on their theoretical back ground is given below.

The Mole Ratio Method: The principle of the method is that a series of solutions is prepared in which the concentration of one component (usually total metal ion concentration, C_M) is kept constant and that of the other varied. The absorbance of the solutions is measured at a suitable wavelength and plotted V_s, the ratio of the variable and constant concentrations. If only one stable complex is formed, which has a selective light absorption, then the absorbance increases approximately linearly with the mole-ratio and then becomes constant. The abscissa of the point of intersection of the two tangents gives the number

of ligand in the complex, if it is the ligand concentration that was varied.

Method of Continuous Variation: The principle of the method is that the mole fractions of the metal ion and ligand are varied between 0 and 1 at constant total concentration and the absorbance of the solutions of different composition is measured. The absorbances are then plotted against the mole fraction, X_L, of the ligand. If only one complex species has been formed, with composition ML_n, and the absorbance is measured at a wavelength where neither the metal ion nor the ligand but only the complex absorbs, then n can be calculated from the abscissa of the maximum of the curve (X_{maX}):

$$n = \frac{X_{maX}}{1-X_{maX}} . \qquad [7]$$

Simple Spectrophotometric Method: The complex formation equilibria involved in the determination of composition of a mixed ligand complex can be represented by the following equations:

$$M + nL \rightleftharpoons ML_n \qquad [8]$$

$$ML_n + mX \rightleftharpoons ML_nX_m \qquad [9]$$

The equilibrium constant for the mixed ligand complex formation equilibrium is given by:

$$K = \frac{[ML_nX_m]}{[ML_n][X]^m} \qquad [10]$$

$$\text{or} \qquad \log \frac{[ML_nX_m]}{[ML_n]} = \log K + m \log [X] \qquad [11]$$

The concentration of the mixed ligand complex, ML_nX_m, is proportional to (A-Amin) and the concentration of the simple complex, ML_n, is proportional to $(A_{max}-A)$ where A is the equilibrium absorbance, A_{min} is the minimum absorbance in the absence of auxiliary ligand, X, and A_{max} is the maximum absorbance in the presence of excess concentration of auxiliary ligand. Equation 11 can then be written as:

$$\log \frac{A-A_{min}}{A_{max}-A} = \log K + m \log [X] \qquad [12]$$

Thus the slope of the curve obtained by plotting $\log (A-A_{min})/(A_{max}-A)$ against log X gives the number, m, of the auxiliary ligand, X.

1.4 Solvent Extraction

Solvent extraction enjoys a favoured position among the separation techniques because of its ease, simplicity, speed, and wide scope. The technique is quite universal and used to get an accurate information on the concentrations and distributions of dissolved trace metals, for instance, in ocean and sea waters which is required in order to understand the geochemical processes controlling their behavior (20). It is also used for sample treatments preceding measurements by atomic absorption spectroscopy either in order to remove the metal ions from interfering

matrix component or in order to preconcentrate them(21). As it is a versatile technique that is widely used in analytical chemistry, extraction procedures have been reported for a majority of elements in the literature (22-24). By using solvent extraction important theoretical problems concerning the composition and stability of soluble as well as insoluble metal complexes can be solved (25-27).

In extraction high selectivity can easily be achieved if the conditions are properly arranged and, whenever necessary, the separation yield can be increased as required by means of successive batch extractions. A further advantage of extraction is that the extract, i.e. the solution of the separated substance in a given organic solvent, usually has same properties on which the determination of the isolated constituent can be based: absorption of light, fluorescence, and radio activity can serve as examples. It is also possible to take advantage of the volatility of the substances which were transferred into the organic phase (e.g. in gas chromatography), or if the extract contains substances which can be readily decomposed, it can be, fed into a flame for flame photometry, atomic absorption or fluorescence.

Solvent extraction (28-34) is based on the distribution of a solute between two essentially immiscible solvents. At equilibrium the ratio of the concentration of the solute in the two phases at a particular temperature remains constant provided the solute has same molecular form in tho two phases. Generally

compounds which are slightly soluble in water but readily soluble in the organic solvent can be usefully extracted. In essentially all metal extraction system some or all of the water molecule co-ordinated to the metal ion must be removed to obtain a species that can be extracted into an organic solvent. On the other hand an uncharged species may be achieved through the neutralization of charge by the association of ions on the basis of purely electrostatic attraction. Hence, the formation of an uncharged species is a probable pre-requisite for extraction of metal ions into the organic solvent.

Organic reagents play an eminent role in extraction separations, because they can react with metal ions to give products having the basic pre-requisite for extractability. These are electrically neutral essentially covalent chelate compounds which are only slightly soluble in water but readily soluble in organic solvents. Most of the organic reagents used for solvent extraction and spectrophotometric determination of metal ions are a particular group of compounds known as chelating agents. A chelating agent contains at least one acid group with a replacable hydrogen atom and a basic co-ordinating donor group in such a position so as to form closed ring compounds on reaction with metal ions, called chelate complexes. The chemical and physical properties of a metal chelate depends upon the nature of the donor atoms and the basic strength of the chelating agent, the nature of the metal ion and the factors inherent in the complex itself such as ring size, resonance, and steric effect. In

general, the most suitable chelating agents are those compounds in which the acid and basic groups are in such a position as to form five or six-membered chelate complexes on reaction with metal ions which are the most stable.

Basic Principles of Extraction of Metal Ions: The extraction of metal, M, with the extraction reagent, HL, forming a chelate, ML_n, soluble in an organic solvent, is expressed by the equilibrium:

$$M_{aq} + nHL_{,org} = ML_{n,org} + nH^+_{aq} \qquad [13]$$

which is characterized by the extraction constant:

$$K_{ex} = \frac{[ML_n]_{org}[H^+]^n_{aq}}{[M]_{aq}[HL]^n_{org}} = \frac{K_{D,M}\,\beta_n}{(K_{D,L}\,BHL)^n} \qquad [14]$$

In liquid-liquid partition, a substance, M, can undergo in both phases various solvation, association, protonation, and, complexation equilibria. For analytical application it is essential to define the partition of the substance irrespective of the particular forms which are encountered in the system. This can be done by expressing the equilibrium ratio of the total analytical concentrations of the substance, M, in the two phases.

$$D_M = \frac{C_{M,org}}{C_{M,aq}} \qquad [15]$$

The completness of transfer of substance, M, in any extractable form into the organic phase is given by the degree of extraction,

E, which is usually expressed in percent:

$$E_M = \frac{100\, C_{M,org}\, V_{M,org}}{C_{A,org}\, V_{A,org} + C_{A,aq}\, V_{A,aq}} = \frac{100\, D_M}{D_M + \frac{V_{aq}}{V_{org}}} \qquad [16]$$

For the metal, M, extracted by HL dissolved in the organic phase the distribution ratio, D_M, is related with the extraction constant according to Equation 17 and 18.

$$D_M = K_{ex} \cdot \left(\frac{[HL]_{org}}{[H^+]_{aq}}\right)^n = \frac{K_{D,M}\, \beta_n}{(K_{D,L}\, \beta_{HL})^n} \left(\frac{[HL]_{org}}{[H^+]_{aq}}\right)^n \qquad [17]$$

$$\log D_M = \log K_{ex} + n \log [HL]_{org} + n\, pH \qquad [18]$$

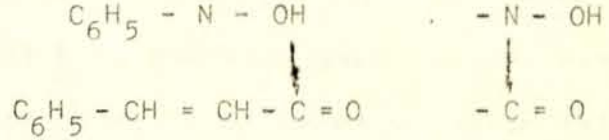
According to Equation 17, the distribution ratio is a function of pH, reagent concentration, dissociation constant of the reagent, stability constant of the extractable complex and the distribution constants of the reagent and the metal. The distribution ratio is also a function of the volume ratio of the aqueous to organic phases according to Equation 16.

The distribution ratio, D_M, can also be influenced by other factors which are not explicitly expressed by the quantities in Equations 16-18. This includes temperature, ionic strength, kinetics of the extraction and solvent. Hence, these are the factors which affect extraction of metalion as chelates and therefore one has to study these effects inorder to develop a method for extraction of a metal ion.

One of the most powerful group of chelating agents used for the solvent extraction and spectrophotometric ditermination of several metal ions in the past twenty five years is hydroxamic acids. In the present investigation N-phenylcinnamohydroxamic acid has been employed as a chelating agent. Hence, its general properties and analytical applications are briefly described in Section 1.5.

1.5 General Properties and Analytical Applications of N-Phenylcinnamohydroxamic Acid

N-Phenylcinnamohydroxamic acid, I, is a typical monobasic and bidentate chelating agent containing a reactive functional group, II, which is capable of forming a five-membered ring on reaction with metal ions.



I II

N-Phenylcinnamohydroxamic acid, PCHA, was first synthesized in 1960 by Majumdar and Mukherjee (35). It is pale-green crystalline solid, m.p. 160 - 161°C. It is stable towards heat, light and air, and can be stored for a long time without deterioration. N-Phenylcinnamohydroxamic acid is a very weak acid and its acid dissociation constant has been found to be 1.6×10^{-9} (36). It is stable towards the action of dilute alkalies and concentrated

hydrochloric acid but decomposes in concentrated sulfuric acid and nitric acid (> 5 N) (37). PCHA, is slightly soluble in water. It is fairly soluble in common organic solvents and its solutions are stable for a long time if stored properly. This storage quality and its stability towards light, heat and air are of great importance from analytical stand point.

N-Phenylcinnamohydroxamic acid was first introduced as an analytical reagent for the gravimetric determination of niobium and tantalum in 1960 (38). Its analytical applications was further extended for the extraction and photometric determination of vanadium (V) (39), zirconium (IV) and hafnium (IV) (40), titanium (IV) and niobium (V) (41) and for the successive extraction and spectrophotometric determination of iron (III), vanadium (V), and uranium (VI) (42). It was also used for the gravimetric determination of uranium (43), and zirconium (44). Recent reports show that PCHA has been used for the extraction and spectrophotometric determination of vanadium (V) as a mixed ligand complex with thiocyanate (45) and p-chlorophenol (46), for the successive extraction and spectrophotometric determination of iron (III) and vanadium (V) (47), and for the simultaneous determination of iron (III) and vanadium (V) by solvent extraction and spectrophotometry (48).

1.6 Aim and Scope of Present Investigation

Several reagents have been recommended for the sectrophotometric determination of vanadium (V) (49-63). Of these reagents comparatively few are well suited as most of these methods lack

sensitivity and suffer from the interference by iron and one or more elements such as copper, nickel, cobalt, chromium and manganese which are commonly associated with vanadium in alloys and complex materials. The non-selectivity of a reagent seriously limits the usefulness of most of the methods. Some reagents are sensitive and selective but they are not commercially available and their synthesis is not simple, hence they are expensive.

In order to further improve the sensitivity and selectivity, the reaction of vanadium (V) with several monobasic and bidentate chelating agents have been studied in detail. It has been found that vanadium (V) reacts with a number of monobasic and bidentate chelating agents to form 1:2 (metal:ligand) colored complexes extractable into various organic solvents. These vanadium complexes contain a basic V = O group and an acidic V-OH group in the same molecule. The basic V = O group of the vanadium complex molecule reacts with acidic substances like carbxylic acids and phenols to give hyper and bathochromic shifts (64-66) and the acidic V-OH group reacts with alcohols giving rise to hipsochromic shift (52-53). N-Phenylbenzohydroxamic acid (67) and its analogues including PCHA (68-76) have been commonly used as selective reagents for the extractive photometric determination of vanadium (V) in concentrated hydrochloric acid media. However, titanium (IV), zirconium (IV), molybdenum (VI), and tungsten (IV) interfere seriously. It has also been shown by some workers (77,78) that extraction is not quantitative because of the partial reduction of vanadium (V) in

concentrated hydrochloric acid media; but this is absent in dilute hydrochloric media (79).

PCHA, a monobasic and bidentate chelating agent, reacts with vanadium (V) to form 1:2 (metal:ligand) complex possessing both the acidic V-OH and the basic V = O group in the same molecule. Thus vanadium (V) - PCHA complex molecule can further reacts with basic substance such as azide and acidic substances such as aldehydes and carboxylic acids which may led to the development of new sensitive and selective methods for the determination of vanadium (V). Hence, the study of these reaction have been the task of the present investigation.

In the present investigation the reaction of vanadium (V) -PCHA complex with azide, benzaldehyde, acetic acid, chloroacetic acid and trichloroacetic acid have been studied spectrophotometrically in detail in order to develop new sensitive and selective methods for the determination of vanadium (V). These studies have resulted in the development of two new methods based on the formation of vanadium (V)-PCHA-azide and vanadium (V)-PCHA -trichloroacetic acid mixed ligand complexes for the determination of vanadium (V) by solvent extraction and spectrophotometry.

2. EXPERIMENTAL

2.1 Apparatus and Reagents

Apparatus: A Beckman Model 24 UV-visible spectrophotometer equipped with 1-cm quartz cells was used for absorbance measurements. A Beckman Chem Mate pH meter was used for the measurements of pH.

Standard Vanadium (V) Solution: A standard solution of vanadium (V) was prepred by dissolving 1.1700 g. ammonium metavanadate (BDH, AnalaR) in distilled water, if necessary acidified with nitric acid, and diluted to 1.0 litre with distilled water. The solution was then standardized volumetrically (14). A working solution was prepared by diluting a suitable aliquot of the standard solution to a known volume with distilled water.

Reagent Solution: N-Phenylcinnamohydroxamic acid, PCHA, was prepared by condensation of N-Phenylhydroxylamine with cinnamoyl chloride at low temperature in diethylether medium made alkaline with aqueous suspension of sodium bicarbonate. The yield was 50%, m.p. 160-161^{o}C (35,39).

A 0.005 M solution of the reagent, PCHA, in ethanol free chloroform was used for the extraction.

Standard Azide Solution: A 1.0 M standard solution was prepared by dissolving sodium azide (Hopikins and Williams) in distilled water.

Standard Trichloroacetic Acid Solution: A 5.0 M standard solution was prepred by dissolving trichloroacetic acid (BDH)

in distilled water.

Solutions of Foreign Ions: Solutions of foreign ions were prepared by dissolving known quantities of reagent grade salts in distilled water to give 10 mg. of the ion in question per millilliter of solution. The solutions were acidified wherever necessary to prevent the hydrolysis. In general nitrate salts were used for the cations and sodium or ammonium salts were used for the anions.

Solutions of Electrolytes: A 2.0 M solution of potassium nitrate (BDH, AnalaR) and potassium chloride (BDH, AnalaR) in distilled water were used for adjusting the ionic strength of the solutions.

Chloroform: Chloroform (Aristar, AnalaR) was washed several times with distilled water to remove the ethanol. It was distilled and dried over anhydrous calcium chloride before being used (80).

Hydrochloric Acid and Ammonia: Dilute solutions (1.0 M) each of hydrochloric acid (BDH, AnalaR) and ammonia (Spectrosol) were used for adjusting the pH of the solutions whenever nessary.

Drying Agent: Anhydrous calcium chloride and anhydrous sodium sulphate were used for drying the distilled solvents and extracts of the colored complexes, respectively.

2.2 Preparation of Sample Solutions

Steel Sample: A weighed amounts of an artificial steel having exactly the same composition as in the British Chemical

Standard Steel No. 64a and 241/1 was transferred into a 400-ml beaker and decomposed with 10 ml of concentrated nitric acid. The mixture was heated to remove the oxides of nitrogen and about 10-15 ml concentrated hydrochloric acid was added to it. The solution was evaporated to almost dryness. About 50 ml of distilled water was added and the solution was boiled. Tungesten was precipitated as tungstic acid. The undissolved silica and tungstic acid were filtered off and washed several times with hot distilled water. The filtrate and washings were collected into a 500 ml volumetric flask and diluted to volume with distilled water. A suitable aliquot was taken for the analysis.

Blood Sample: A 5 ml aliquot of blood Sample 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 treated with 10 ml of the acid mixture in a ratio of 3:1:1 (nitric:sulfuric:perchloric) and heated over the bunsen burner until perchloric acid was evaporated and dense white fumes of sulfur trioxide appear. The heating was continued for about two hours. It was cooled and the residue was boiled with 50 ml of 0.10 M hydrochloric acid for 30 minutes. The solution was cooled and transferred quantitatively to a 100-ml volumetric flask. A dilute solution of potassium permaganate was added to the solution to ensure the oxidation of vanadium (IV) to vanadium (V) and diluted to volume. A suitable aliquot of the sample solution was taken for the analysis.

2.3 General Procedure for Extraction of Vanadium (V)

Vanadium (V)-N_3-PCHA System

An aliquot of the solution containing 25-175 µg of vanadium (V) was transferred into a 100-ml separatory funnel and 10 ml of 1.0 M solution of azide was added to it. The solution was diluted to 25 ml with distilled water and acidity was adjusted to 0.1 - 1.0 M with 10 M hydrochloric acid. A 10 ml aliquot of 0.005 M of reagent solution in chloroform was added to the funnel and the mixture was shaken vigorously for 3-4 minutes. 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 diluted to volume with chloroform. The absorbance of the colored solution was measured at 560 nm against chloroform.

Vanadium (V)-TCAA-PCHA System: An aliquot of the solution containing 25 - 175 µg of vanadium (V) was transferred into a 100-ml separatory funnel. The acidity of the solution was adjusted to 2-3 M with trichloroacetic acid, TCAA, and the volume of the aqueous phase to 10 ml with distilled water. A 10 ml of aliquot of 0.005 M PCHA solution in chloroform was added to the funnel and then proceeded as in V(V)-N_3-PCHA system. The absorbance was measured at 542 nm against the reagent blank.

For calibration, 0.1, 0.2, 0.3, 0.4, 0.5 ml of standard solution (0.01 M V(V)) were used through the procedure.

2.4 Procedure for Studying the Effect of Variables

The effect of several experimental variables on the extraction and determination of vanadium (V) with PCHA in the presence of azide and trichloracetic acid was studied by following the general procedure. The effect of a particular variable was studied by keeping all the variables constant except the one under study.

2.5 Procedure for Determination of Composition of Complexes

Mole Ratio Method

A series of solutions was prepared for each system in which the concentration of vanadium (V) and auxiliary ligands, the acidity, and ionic strength were kept constant and the concentration of PCHA was varied under exactly similar conditions. The complexes were extracted by the general procedure. The absorbances of the colored extracts were measured at the respective λ_{max} against the reagent blank and plotted against the mole ratio of metal ion to PCHA. Two straight lines were drawn from the two parts of the curve which intersects each other at a mole ratio of vanadium to PCHA.

Continuous Variation Method: In the continuous variations method a series of solutions was prepared for each system in which the mole fractions of the metal ion and PCHA were varied between 0 and 1 at constant total concentration under exactly similar conditions. The concentration of azide or trichloroacetic acid was also kept constant excess throughout the series.

The complexes were extracted by the general procedure and the absorbances of the colored extracts were measured at the respective λ_{max} for the two systems against the reagent blank. The absorbances are then plotted against the mole fraction of the metal ion.

Simple Spectrophotometric Method: To determine the ratio of vanadium (V) to azide or trichloroacetic acid in the mixed legand complexes, by absorptiometric method a series of solutions was prepared for each system in which the concentrations of vanadium (V) and PCHA were kept constant and the concentration of azide or trichloroacetic acid was varied under exactly similar conditions. The complexes were extracted by the general procedure and the absorbances of the colored extracts were measured at the respective λ_{max} against the reagent blank.

2.6 Procedure for Studying the Effect of Foreign Ions

The effect of foreign ions was studied by adding known amount of a desired ion to solutions containing 100 µg of vanadium (V). The concentration of PCHA and auxiliary ligands were kept constant excess and the acidity of the solutions were adjusted in the optimum concentration range. Then, vanadium (V) was extracted and determined by the general procedure.

3. RESULTS AND DISCUSSION

3.1 Reaction Conditions and Absorption Spectra

The reaction of vanadium (V) with PCHA in the absence and presence of auxiliary ligand: azide, benzaldehyde, acetic acid, chloroacetic acid and trichloroacetic acid have been studied by solvent extraction and spectrophotometry.

Vanadium (V) reacts with PCHA to form a binary complex which is readily extractable into common organic solvents. However the complex is not very stable and decomposes upon standing. The reddish brown colored complex extracted into chloroform exhibts two absorption bands in the visible region. An intense and sharp absorption band at around 370 nm and a relatively weak and broad absorption band at around 505 nm which can be assigned to the π-π^* transition in the ligand and the charge transfer transition from the ligand to the metal, respectively (5). It has been found that vanadium (V), as binary vanadium (V)-PCHA complex, is completely extracted into chloroform from the aqueous phase in the acidity range of 0.03-0.5 M HCl.

At higher pH extraction of vanadium (V) from the aqueous phase was found to be incomplete indicating the incompletness of complex formation with PCHA. The possible reason for the incomplete complex formation is that the nature and composition of vanadium (V) in aqueous solution depends on the pH of the medium (1). Vanadium (V) exists as colorless ortho vanadate, VO_4^{3-}, in strongly alkaline solution, i.e. at pH 13. Lowering

the pH of the solution initiates the poly condensation processes and the formation of the so-called isopolyanions. Thus, in the pH range 13-8 the yellow divanadate, $V_2O_7^{4-}$, is encountered. Between pH 8 and 6 the bright yellow tetravanadate, $V_4O_{12}^{4-}$, and, in acidic medium of pH 6-4 the orange decavanadate, $V_{10}O_{28}^{6-}$, are formed. At around pH 2 orange red V_2O_5 is precipitated. In strongly acidic medium the oxide dissolves again yielding the yellow vanadyl cation, VO_2^+. The chemical reaction have been studied by a variety of physical methods including Raman spectroscopy (81), but the nature of the species formed has been, and to some extent still is, controversial. The available data seem most consistent with the following main chemical reactions:

$$V_2O_5 + 6OH^- \xrightarrow{pH\ 13} 2VO_4^{3-} + 3H_2O \qquad [19]$$

$$2VO_4^{3-} + 2H^+ \xrightleftharpoons{pH\ 13\text{-}8} V_2O_7^{4-} + H_2O \qquad [20]$$

$$2V_2O_7^{4-} + 4H^+ \xrightleftharpoons{pH\ 8\text{-}6} V_4O_{12}^{4-} + 2H_2O \qquad [21]$$

$$5V_4O_{12}^{4-} + 8H^+ \xrightleftharpoons{pH\ 6\text{-}4} 2V_{10}O_{28}^{6-} + 4H_2O \qquad [22]$$

$$V_{10}O_{28}^{6-} + 6H^+ \xrightleftharpoons{pH\ 4\text{-}2} 5V_2O_5(aq) + 3H_2O \qquad [23]$$

$$V_2O_5 + 2H^+ \xrightleftharpoons{pH < 2} 2VO_2^+ + H_2O \qquad [24]$$

Equations 19-24 suggest that vanadium (V) exists in aqueous solution as different species at different pH. Consequently the nature and composition of the complex species formed with PCHA are also

expected to be different as indicated from the differences in absorption spectra at different pH (Fig. 1).

At higher acidity (2.5-7.5 M) a hyper and bathochromic shift of the absorption band (L → M) has been observed. The band at 505 nm (L → M) was shifted to 540 nm with increased intensity while the band at 370 nm practically remained unchanged. This is due to the formation of a stable mixed ligand complex with HCl (64). At very high concentration of HCl, i.e. > 7.5 M, the position of both the absorption bands remained the same while the intensity began to decrease due to the protonation of the ligand (Fig. 2).

The spectrum of V(V)-PCHA complex has been found to be further affected by the presence of alcohol. The absorption band at 505 was shifted to shorter wavelength with an increase in the intensity while the absorption band at 370 nm remained unaffected. The change in the absorption band associated with charge transfer electronic transition of the V(V)-PCHA complex in the presence of ethanol is due to the esterification of the complex containing an -OH group in the vanadium (V)-PCHA complex molecule (52).

The simple V(V)-PCHA complex was found to react with azide, benzaldehyde, acetic acid, chloroacetic acid and trichloroacetic acid to form mixed ligand complexes. The formation of a mixed ligand complex in each system was evident from:

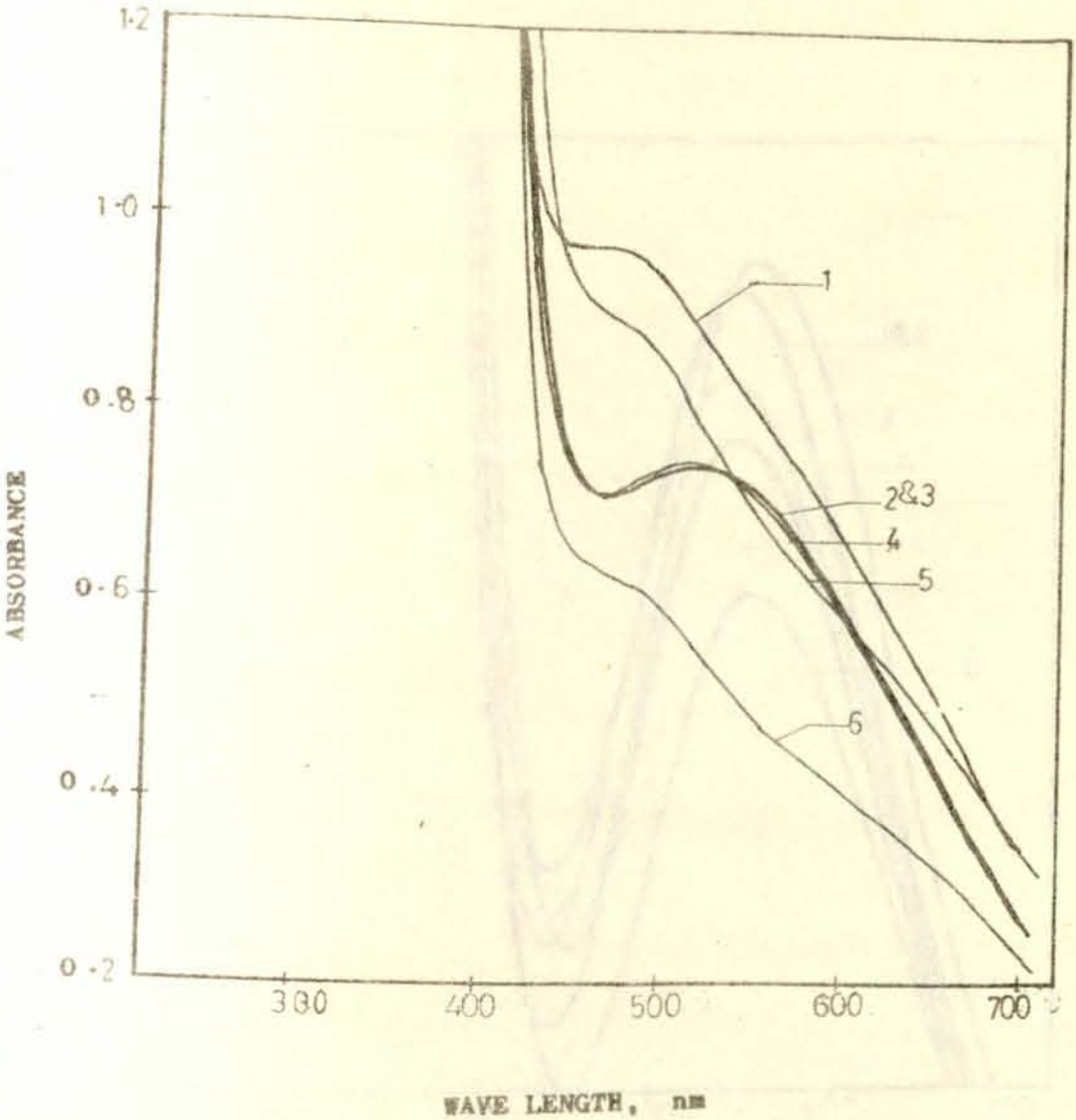


Fig.1 Absorption spectra of V(V)-PCHA complex at Lower Acidity Range Against Chloreform, for PH 6 (6), PH 4 (5) PH 3 (3), PH 2 (1), PH 1.5 (2), PH 1(3), 0.5 M HCl (4) [V (V)] = 2 X 10^{-4}M.

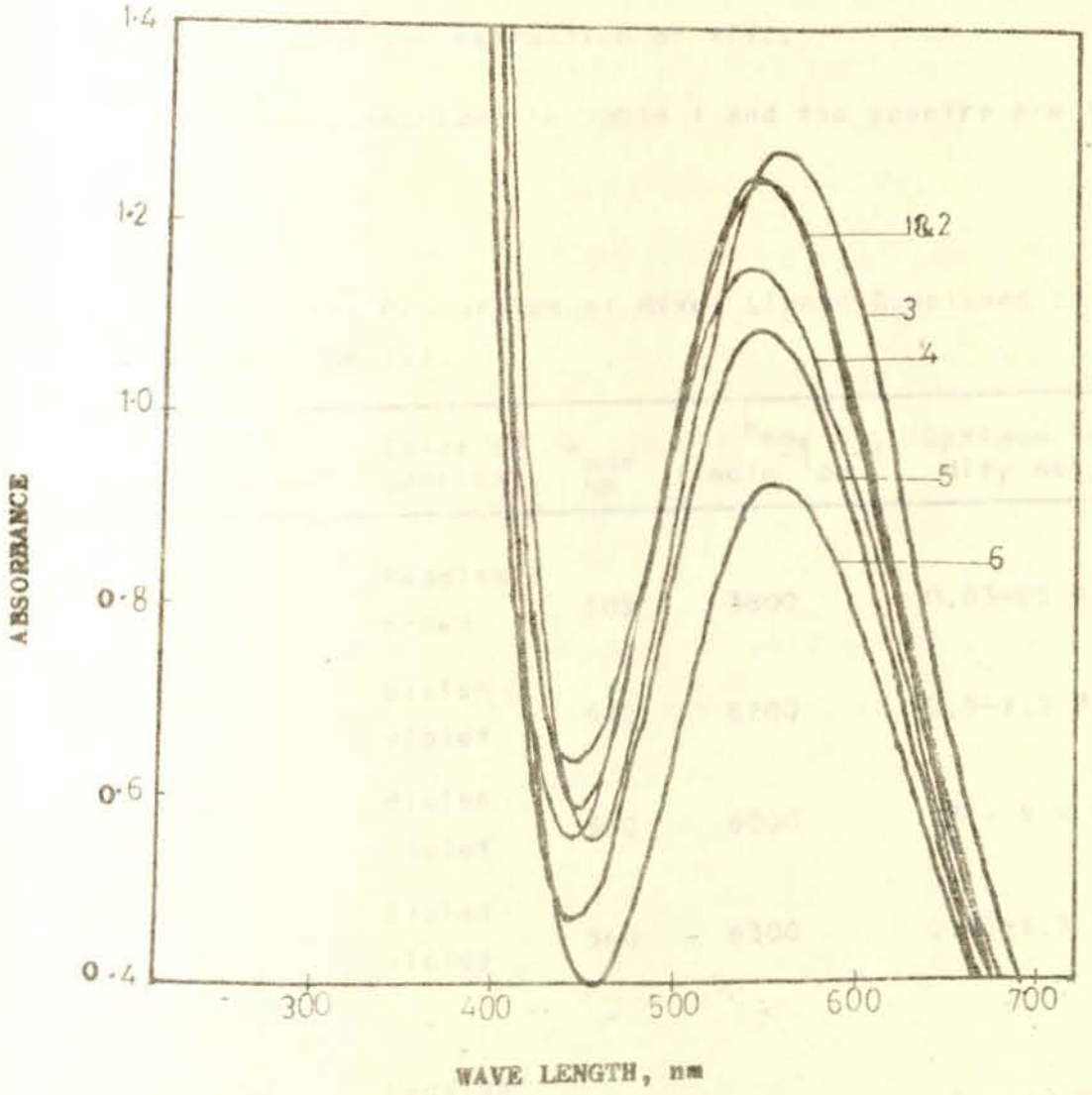


Fig. 2 Absorption Spectra of V(V)-PCHA Complex at Higher Acidity Range Against Chloroform, for 2.0M HCl (4), 2.5 M HCl (1), 7.5 M HCl (2), 8.0 M HCl (5), 9 M HCl (6), 0.5 M HCl in presence of N_3^- (3), [V(V)] = 2 X 10^{-4}M.

i) the changes in the wavelength of maximum absorption;

ii) the variations in the molar absorptivity at the respective λ_{max};

iii) the difference in the acidity ranges of the aqueous phase for the complete extraction of V(V).

The results are summarized in Table I and the spectra are shown in Fig. 3-9.

Table I. Spectral Properties of Mixed Ligand Complexes of Vanadium (V).

Auxiliary Ligand	Color of Complex	λ_{max} nm	ε_{max} l mole^{-1} cm^{-1}	Optimum Acidity Range
None	Reddish brown	505	3800	0.03-05 M CHI
HCl	Bluish violet	540	6200	2.5-7.5 M HCl
Benzaldehyde	Bluish violet	550	6000	3 - 4 M HCl
Azide	Bluish violet	560	6300	0.01-1.5 M HCl
*Acetic Acid	-	-	-	-
Chloroacetic Acid	Reddish violet	530	6680	3 - 10 M CAA
Trichloroacetic Acid	Reddish violet	542	7750	2 - 5 M TCCA

*λ_{max} and ε_{max} varies with concentration (1-10 M).

The vanadium (V)-PCHA-N_3 and the vanadium (V)-PCHA-TCAA (or CAA) ternary complex systems have been found to be the most sensitive and stable among the mixed ligand complexes studied. At the same time V(V)-PCHA-N_3 complex is completely extractable at the lower acidity range with respect to HCl and V(V)-PCHA-TCAA (or CAA) is completely extractable in the absence of HCl into common organic solvents. This is the advantage of both the systems for the precise determination of vanadium (V) since, there is no danger of reduction of vanadium (V) to vanadium (IV) in the dilute HCl or in its absence (77,78). Hence, these two systems underlie the basis for the development of two new solvent extraction and spectrophotometric methods for the determination of vanadium (V). Therefore, the two systems have been studied in detail.

The absorption spectrum of vanadium (V)-PCHA binary complex was found to be affected in the presence of azide. The absorption band at 505 nm was shifted to 560 nm and the one at 370 nm practically remained unchanged. The optimum acidity range of the aqueous phase for the complete extraction of vanadium (V) in the presence of azide was found to be 0.01-1.5 M with respect to HCl. At lower acidity different absorption spectra have been found as already expected since vanadium (V) exists in aqueous solution as different speci.s leading to the formation of different complex species. At higher acidity there was a shift in λ_{max} from 560 to 540 nm because of the protonation of azide and the formation of V(V)-PCHA-HCl complex retarding the formation

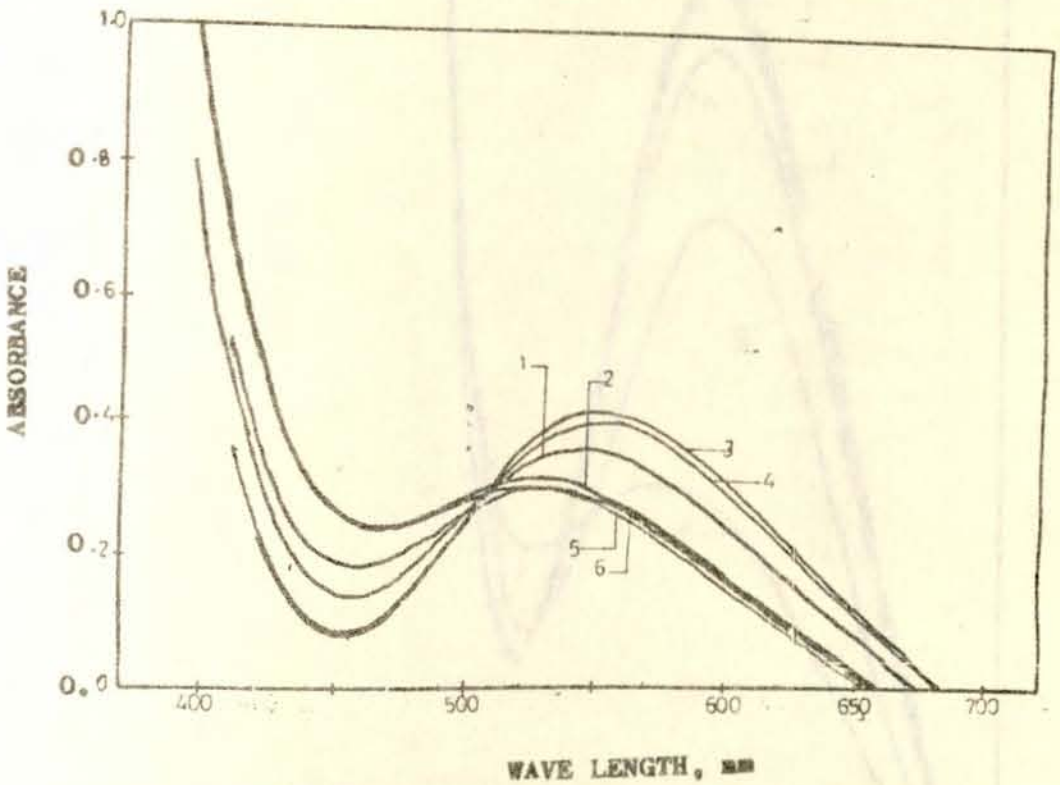


Fig. 3 Absorption Spectra of V(V)-PCHA Complex in the presence of Benzaldehyde Against Chloroform, for 0.5 M HCl (6), 1 M HCl (5), 2 M HCl (2), 3 M HCl (3), 4 M HCl (4), 5 M HCl (1), [V (V)] = 6.7×10^{-5} M.

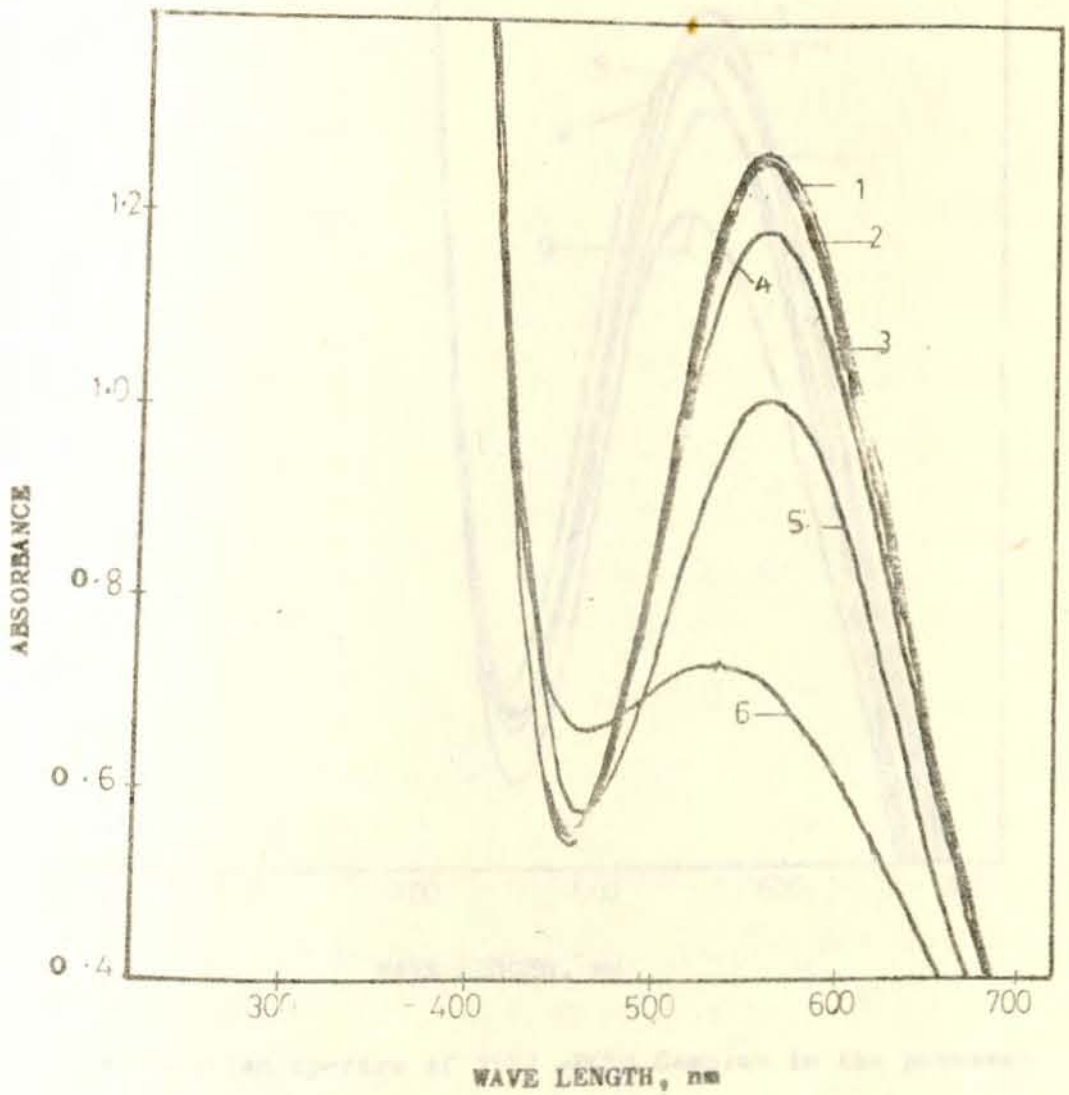


Fig. 4 Absorption Spectra of V(V) - PCHA Complex in the presence of Azide at Lower Acidity Range Against Chloroform for, PH 1 (1), PH 1.5 (2), PH 2 (3), PH 2.5 (4), PH 3 (5), PH 6 (6). [V(V)] = 2 X 10^{-4}M.

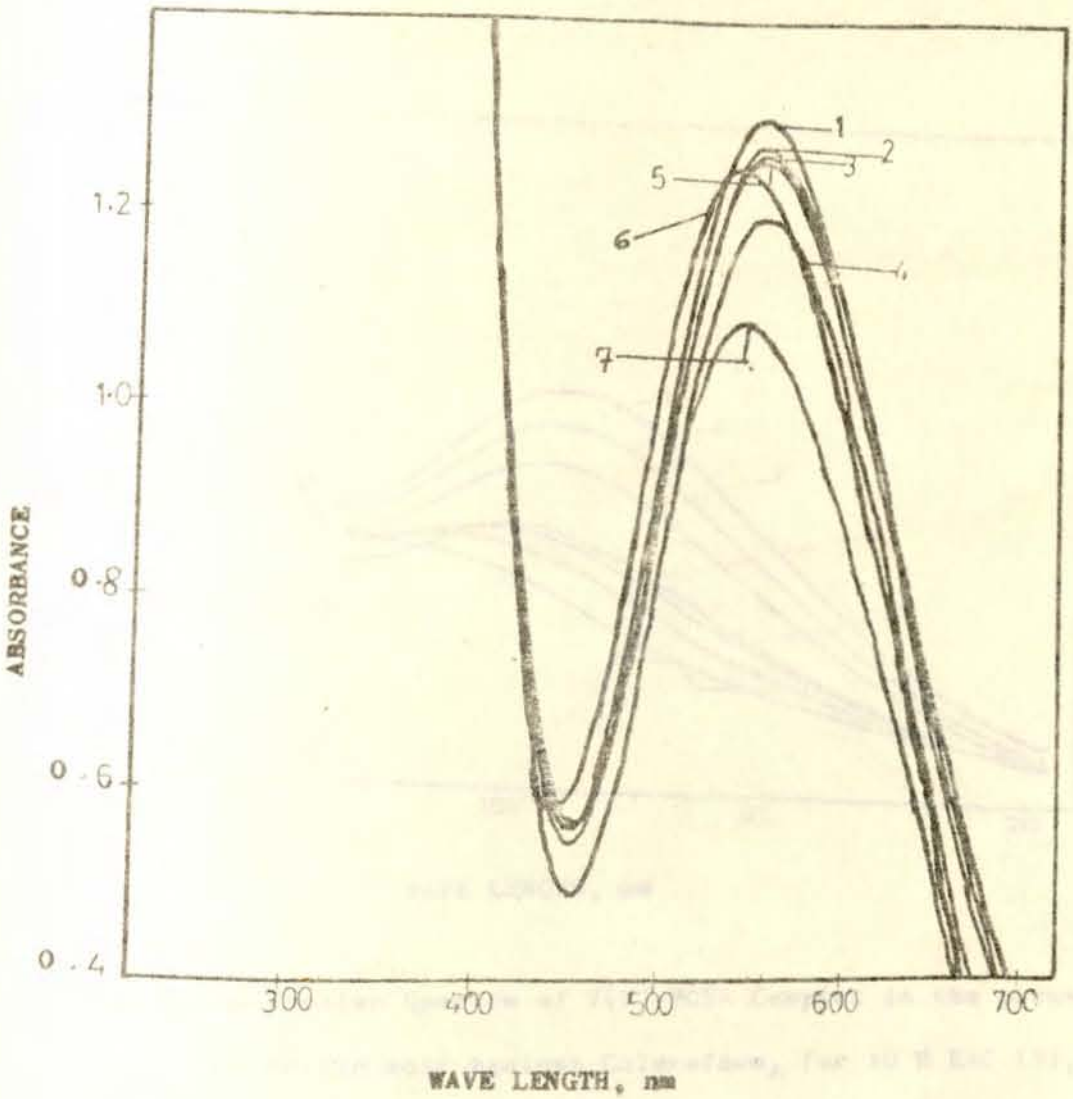


Fig. 5 Absorption Spectra of V(V) -PCHA Complex in the presence of Azide at Higher Acidity Range Against Chloroform for, 0.5 M HCl (1), 1 M HCl (2), 1.5 M HCl (3), 2 M HCl (5), 2.5 M HCl (4), 4 M HCl (6), 8 M HCl (7), [V(V)] = 2 X 10^{-4}M.

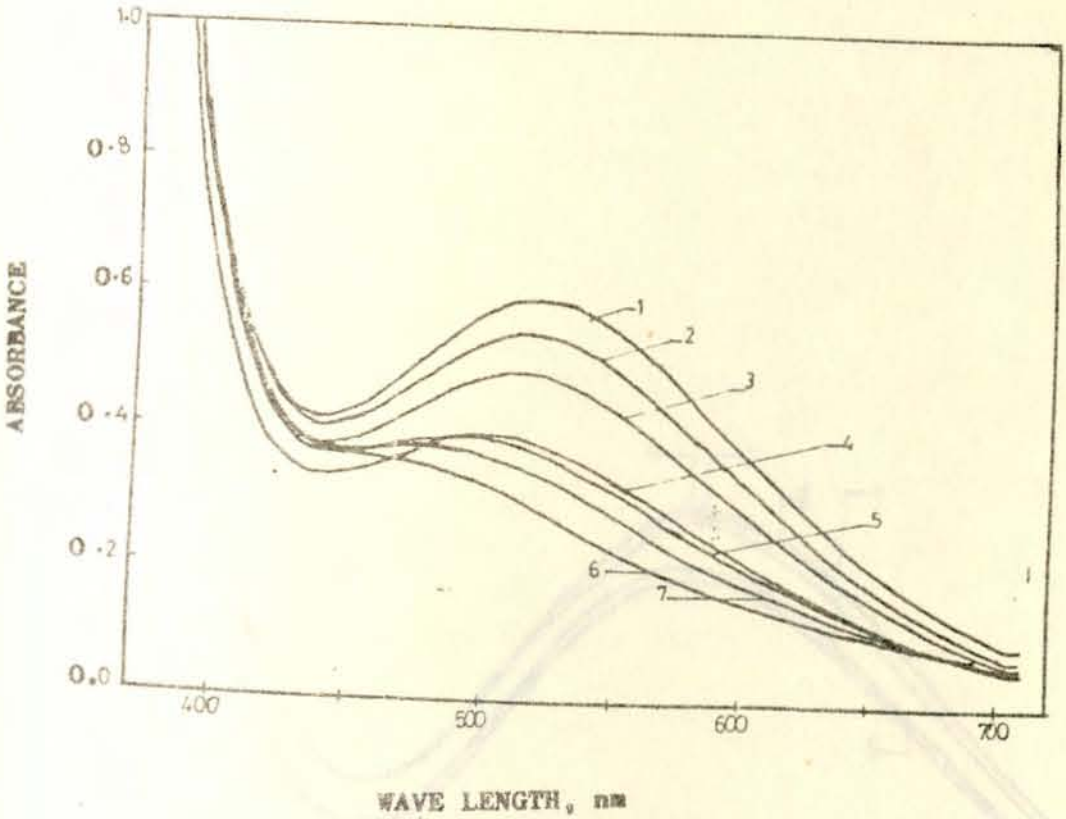


Fig. 6 Absorption Spectra of V(V)-PCHA Complex in the presence of acetic acid against Chloroform, for 10 M HAC (1), 8 M HAC (2), 6 M HAC (3), 4 M HAC (4), 3 M HAC (5), 2 M HAC (7), 1 M HAC (6), $[V(V)] = 1 \times 10^{-4}$M.

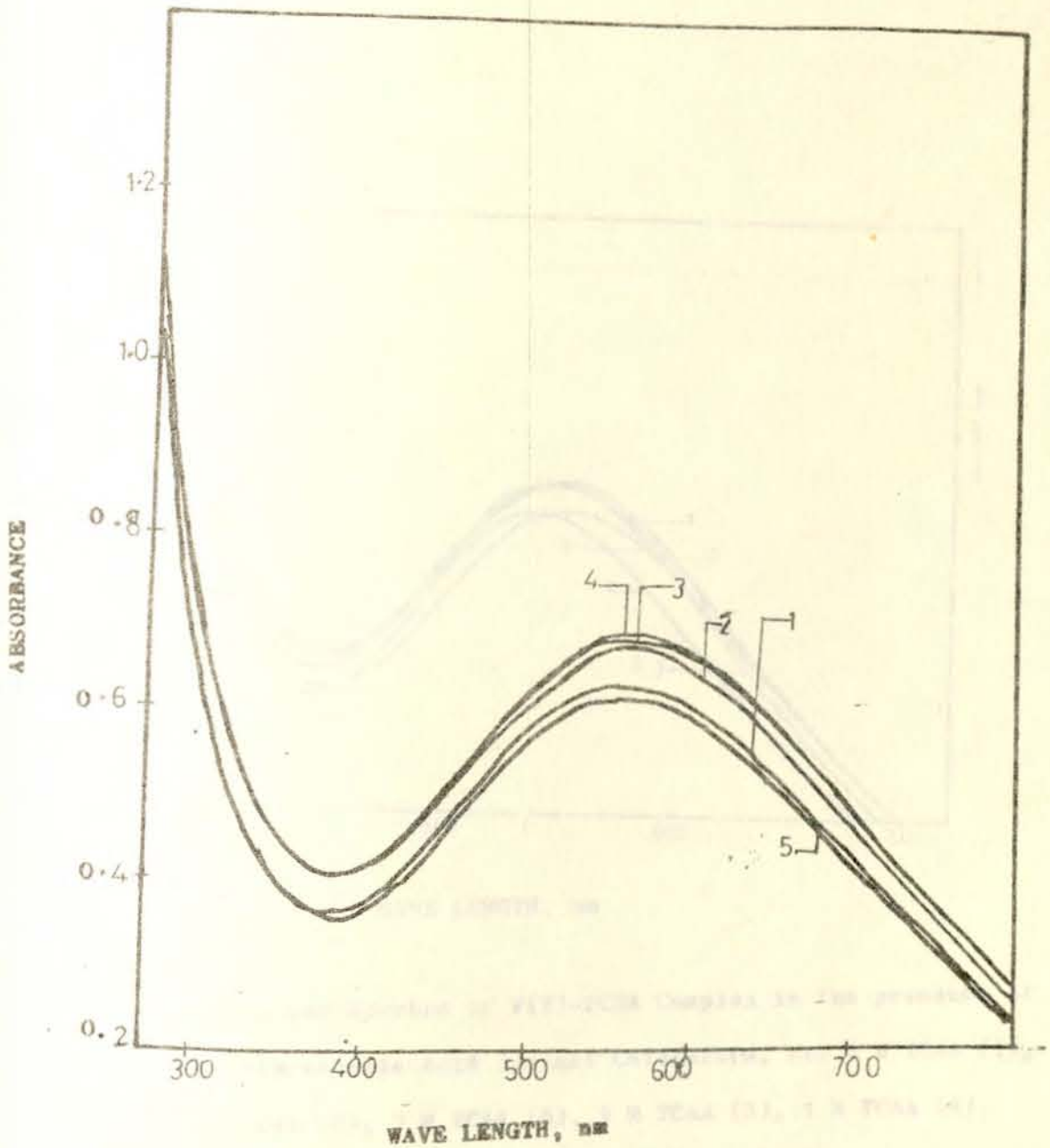


Fig. 7 Absorption Spectra of V(V)-PCHA Complex in the presence of Chloroacetic acid Against Chloroform, for 1 M CAA (5), 2 M CAA (2), 3 M CAA (3), 8 M CAA (1), 10 M CAA (4), $[V(V)] = 1 \times 10^{-4}$ M.

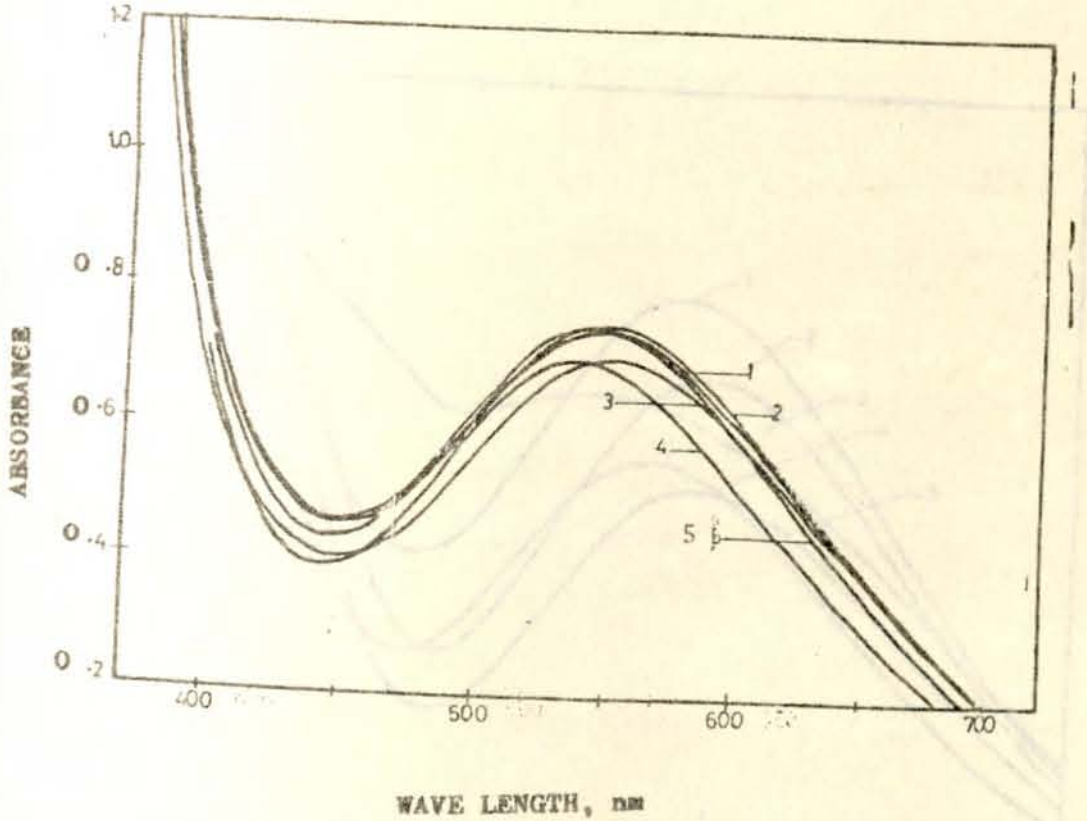


Fig. 8 Absorption Spectra of V(V)-PCHA Complex in the presence of Trichloroacetic Acid Against Chloroform, for 5 M TCAA (1), 4 M TCAA (2), 3 M TCAA (5), 2 M TCAA (3), 1 M TCAA (4), [V (V)] = 1 X 10^{-4}M.

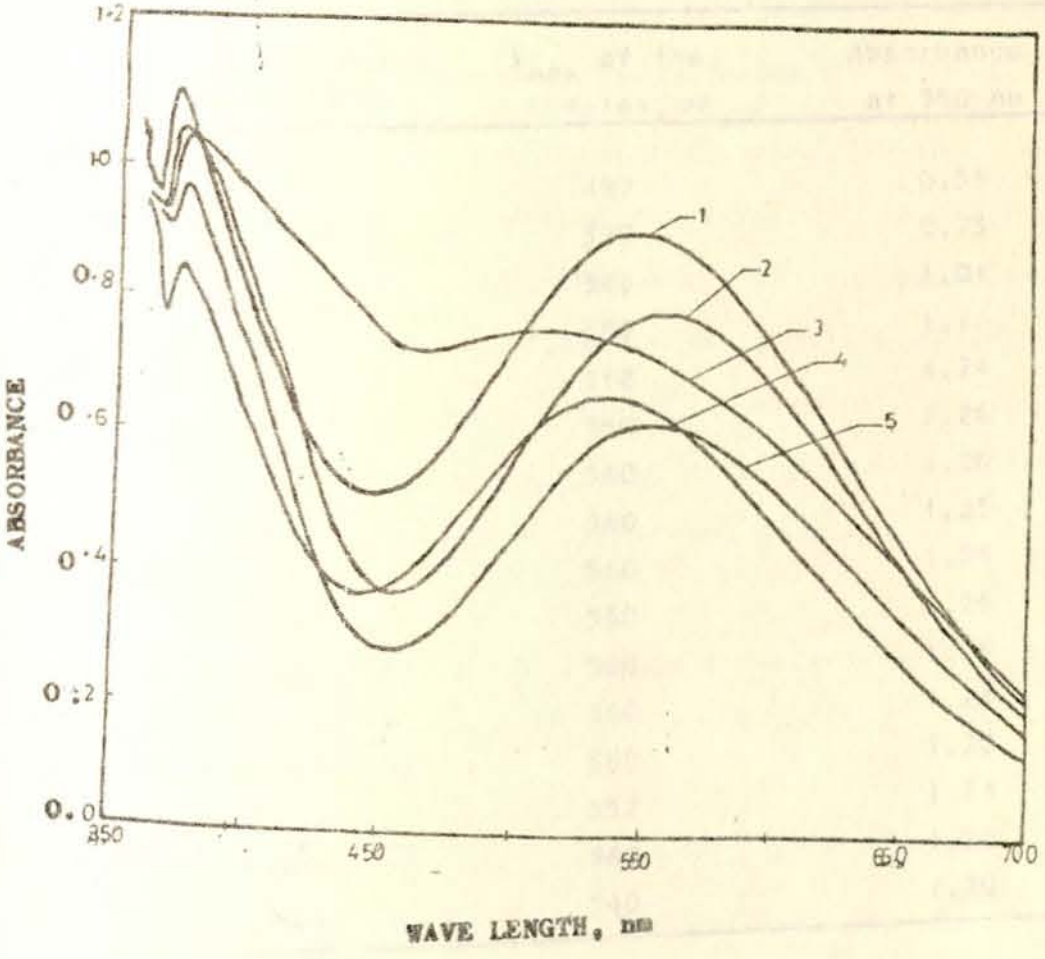


Fig. 9 Absorption Spectra of Mixed Ligand Complexes* of Vanadium (V) Against Reagent blank, for V(V) -PCHA-TCAA (1), [V(V)] = 1.16 X 10^{-4}M; V(V)-PCHA-N_3(2), [V(V)] = 1.6 X 10 [V(V)]-PCHA in 0.5 M HCl (3), [V(V)] = 2 X 10^{-4}M; V(V)-PC (4), [V(V)] = 1 X 10^{-4}M; V(V)-PCHA-Benzaldehyde (5), [V(V)] = 1 X 10^{-4}M.

* Acidity is within optimum experimental range.

of the vanadium (V)-PCHA-N_3 mixed ligand complex. The results are given in Table 2.

Table 2. Effect of Acidity of the Aqueous Phase on the Absorption Spectrum and Extraction of Vanadium (V) in the Presence of Azide. $[V(V)] = 2 \times 10^{-4}$ M, $[N_3^-] = 0.5$ M.

Acidity of the Aqueous Phase	λ_{max} of the Complex, nm	Absorbance at 560 nm
pH 8.0	487	0.56
pH 6.0	527	0.75
pH 4.0	545	1.01
pH 3.0	552	1.18
pH 2.5	558	1.24
pH 2.0	560	1.26
pH 1.5	560	1.26
pH 1.0	560	1.25
0.5 M HCl	560	1.26
1.0 M HCl	560	1.26
1.5 M HCl	560	1.26
2.0 M HCl	560	1.23
2.5 M HCl	560	1.20
3.0 M HCl	552	1.13
4.0 M HCl	540	1.20
6.0 M HCl	540	1.20

The absorption spectra of V(V)-PCHA-N_3 mixed ligand complex at the optimum acidity range has been found to be similar both in the absence and presence of ethanol. These results indicate the absence of an -OH group in the mixed ligand complex molecule. Thus it seems that the -OH group is replaced by azide during the mixed ligand complex formation.

The reaction and extraction of vanadium (V) with PCHA has been studied in acetic acid, chloroacetic acid and trichloroacetic acid media in the absence of HCl. It has been found that the extraction of vanadium (V) is incomplete from 1-10 M acetic acid medium. The complex exhibited different absorption spectra at different concentrations of the acid and it was not stable.

The extraction of vanadium (V)-PCHA complex was found to be complete in the concentration range 3-10 M and 2-5 M of chloroacetic acid and trichloroacetic acid, respectively, in the aqueous phase. The charge transfer absorption band of the simple V(V)-PCHA complex was greatly intensified and shifted to 530 and 542 nm in the chloroacetic acid and trichloroacetic acid systems, respectively, while the π-π^* transition band was only slightly affected.

Below the optimum acidity range different absorption spectra were found at different acidities of the aqueous phase in both the systems; while above the optimum acidity range phase separation was difficult in both the systems due to increasing miscibility of the organic (e.g. chloroform) and aqueous phases. The results are given in Table 3 and 4.

Table 3. Effect of Concentration of Chloroacetic Acid in the Aqueous Phase on the Absorption Spectrum and Extraction of Vanadium (V). [V(V)] = 1×10^{-4} M, [PCHA] = 2×10^{-3} M.

[CAA]	λ_{max} of the Complex, nm	Absorbance at 530 nm
1.0	525	0.625
2.0	527	0.640
3.0	530	0.664
4.0	530	0.668
5.0	530	0.668
6.0	530	0.678
7.0	530	0.675
8.0	530	0.670
10.0	530	0.672

The absorption spectrum of the reagent (PCHA), has been studied in the visible region. The reagent 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 was necessary for the measurements of absorbance at wavelengths shorter than 500 nm; while it was not necessary at larger wavelengths.

Table 4. Effect of Concentration of Trichloroacetic Acid in the Aqueous Phase on the Absorption Spectrum and Extraction of Vanadium (V). $[V(V)] = 1 \times 10^{-4}$ M, $[PCHA] = 2 \times 10^{-3}$ M.

[TCAA]	λ_{max} of the Complex, nm	Absorbance at 542 nm
0.1	527	0.523
1.0	537	0.714
1.5	537	0.747
2.0	542	0.769
3.0	542	0.769
4.0	542	0.764
5.0	542	0.770
*6.0	-	-
*8.0	-	-

*No phase separation.

As already mentioned, all the mixed ligand complexes of V(V) with PCHA and the auxiliary ligands in the foregoing discussions exhibited two absorption bands. Although, the absorption band associated with the π-π^* transition was relatively intense than the band associated with the charge transfer in each system, the later was selected for absorbance measurements due to the fact that the reagent, PCHA, absorbs strongly in the shorter wavelength region.

Several organic solvents such as chloroform, carbontetrachloride, benzene, toluene, chlorobenzene odichloro benzene and xylene were found to extract all the complexes from the aqueous phase. The absorption spectra of the individual complexes were found to be similar in all the nonpolar organic solvents. However, variations in absorbance values were noticed. Chloroform was found to be the most suitable solvent for extraction of the vanadium (V)-PCHA-N_3 and the vanadium (V)-PCHA TCAA (or CAA) complexes, because the quantitative extraction of both the complexes is readily accomplished in it. It was also preferred because of its higher density and relatively higher solubility of PCHA in it than in other solvents.

3.2 Composition of Complexes

The composition of vanadium (V)-PCHA-N_3 and vanadium (V)-PCHA-TCAA complexes have been determined by different spectrophotometric methods. The mole ratio (17) and continuous variations (18) methods were used to determine the ratio of vanadium (V) to PCHA while a simple spectrophotometric method (19) was used to determine the ratio of vanadium (V) to azide or trichloroacetic acid.

The results obtained by the mole ratio method indicated the ratio of vanadium (V) to PCHA to be 1:2 in the two complexes. The results are given in Tables 5 and 6 and the curves are shown in Fig. 10 and 11.

Table 5. Results of Mole Ratio Method for V(V)-PCHA-N_3 System [V(V)] = 1×10^{-4} M, [N_3^-] = 0.5 M, [HCl] = 0.1 M

[V(V)] : [PCHA]	Absorbance at 560 nm
1:1	0.332
1:2	0.470
1:3	0.569
1:4	0.593
1:5	0.613
1:6	0.629
1:8	0.630
1:10	0.630
1:20	0.628
1:50	0.629

Table 6. Results of Mole Ratio Method for V(V)-PCHA-TCAA System. [V(V)] = 8×10^{-5} M, [TCAA] = 3 M

[V(V)] : [PCHA]	Absorbance at 542 nm
1:1	0.290
1:2	0.481
1:3	0.561
1:4	0.595
1:6	0.618
1:10	0.620
1:20	0.619
1:50	0.618

In the continuous variations method the maximum absorbance was observed at the mole fraction of 0.33 of the metal ion in

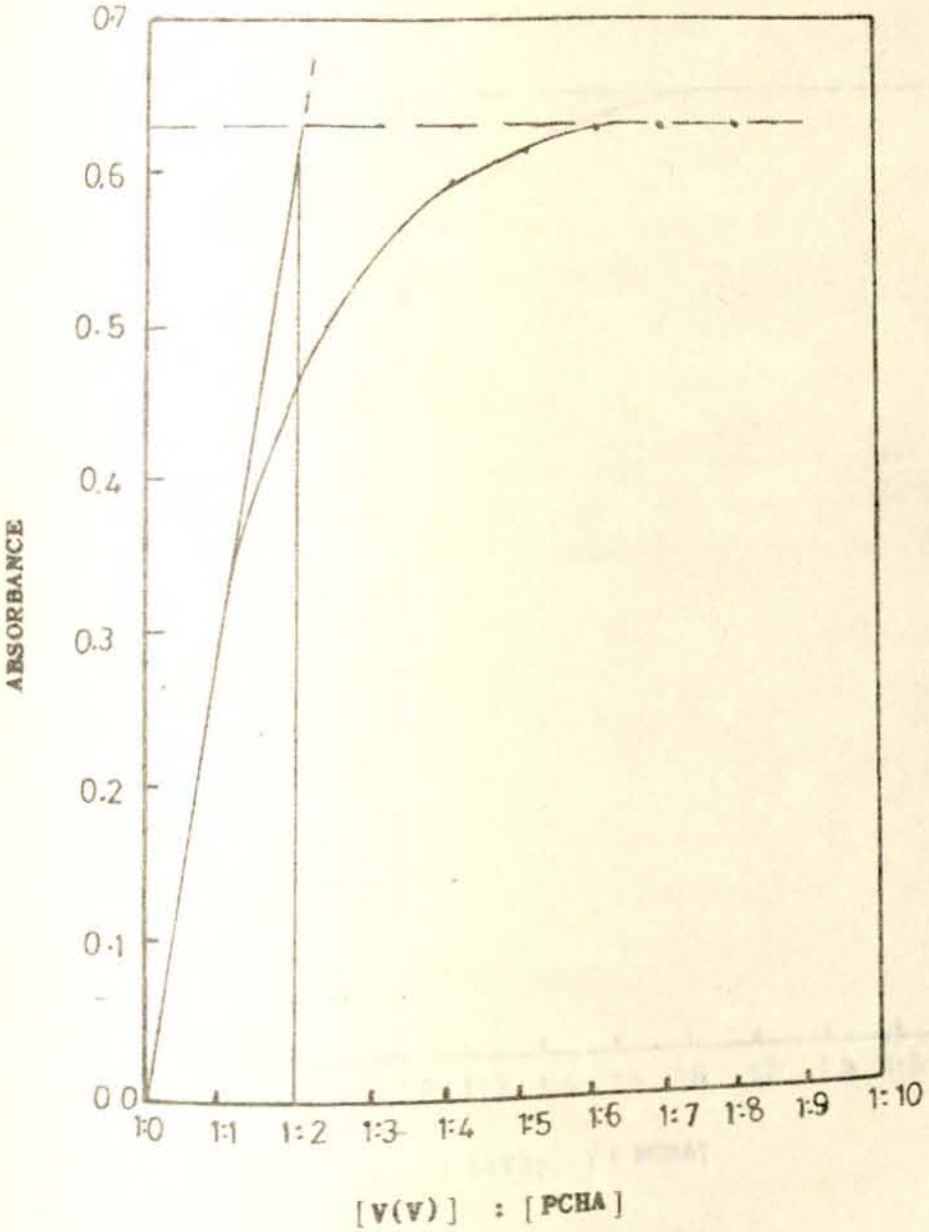


Fig. 10 Mole ratio method curve for V(V)-PCHA-N_3 system.

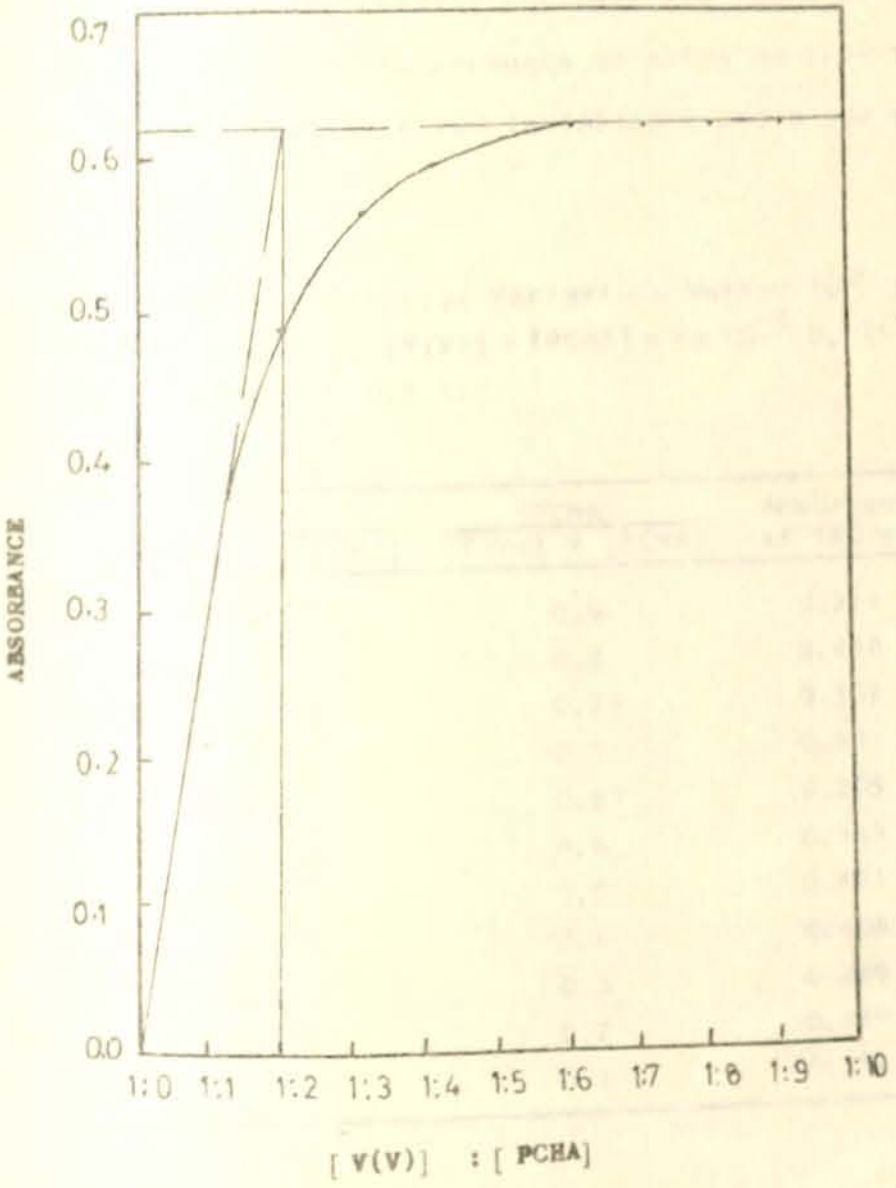


Fig. 11 Mole ratio method curve for V(V)-PCHA-TCAA system

both the systems. These results indicate the ratio of vanadium (V) to PCHA to be 1:2 in the presence of azide or trichloroacetic acid. The results are given in Tables 7 and 8 and the curves are shown in Fig. 12 and 13.

Table 7. Results of Continuous Variations Method for V(V)-N_3^--PCHA System. [V(V)] + [PCHA] = 4×10^{-4} M, [N_3^-] = 0.5 M, [HCl] = 0.1 M.

$\frac{[V(V)]}{[V(V)] + [PCHA]}$	$\frac{[PCHA]}{[V(V)] + [PCHA]}$	Absorbance at 560 nm
0.1	0.9	0.241
0.2	0.8	0.430
0.25	0.75	0.532
0.3	0.7	0.581
0.33	0.67	0.605
0.4	0.6	0.563
0.5	0.5	0.471
0.6	0.4	0.408
0.7	0.3	0.289
0.8	0.2	0.189
0.9	0.1	0.156

Table 8. Results of Continuous Variations Method for V(V)-PCHA-TCAA System. $[V(V)]+[PCHA] = 4\times10^{-4}$ M, [TCAA]=3M

$\frac{[V(V)]}{[V(V)]+[PCHA]}$	$\frac{[PCHA]}{[V(V)]+[PCHA]}$	Absorbance at 542 nm
0.1	0.9	0.302
0.2	0.8	0.573
0.25	0.75	0.702
0.3	0.7	0.781
0.33	0.67	0.814
0.4	0.6	0.778
0.5	0.5	0.685
0.6	0.4	0.555
0.7	0.3	0.437
0.8	0.2	0.298
0.9	0.1	0.150

The ratio of vanadium (V) to azide or trichloroacetic acid was determined by simple spectrophotometric method. The quantity $\log \frac{(A-A_{min})}{(A_{max}-A)}$ were calculated and plotted as a function of log $[N_3^-]$ or log [TCAA] in the two systems, respectively. The slope of the curves were found to be near unity in both cases which indicate, the ratio of vanadium (V) to azide and vanadium (V) to trichloroacetic acid to be 1:1. The results are given in Tables 9-12 and the curves are shown in Fig. 14 and 15.

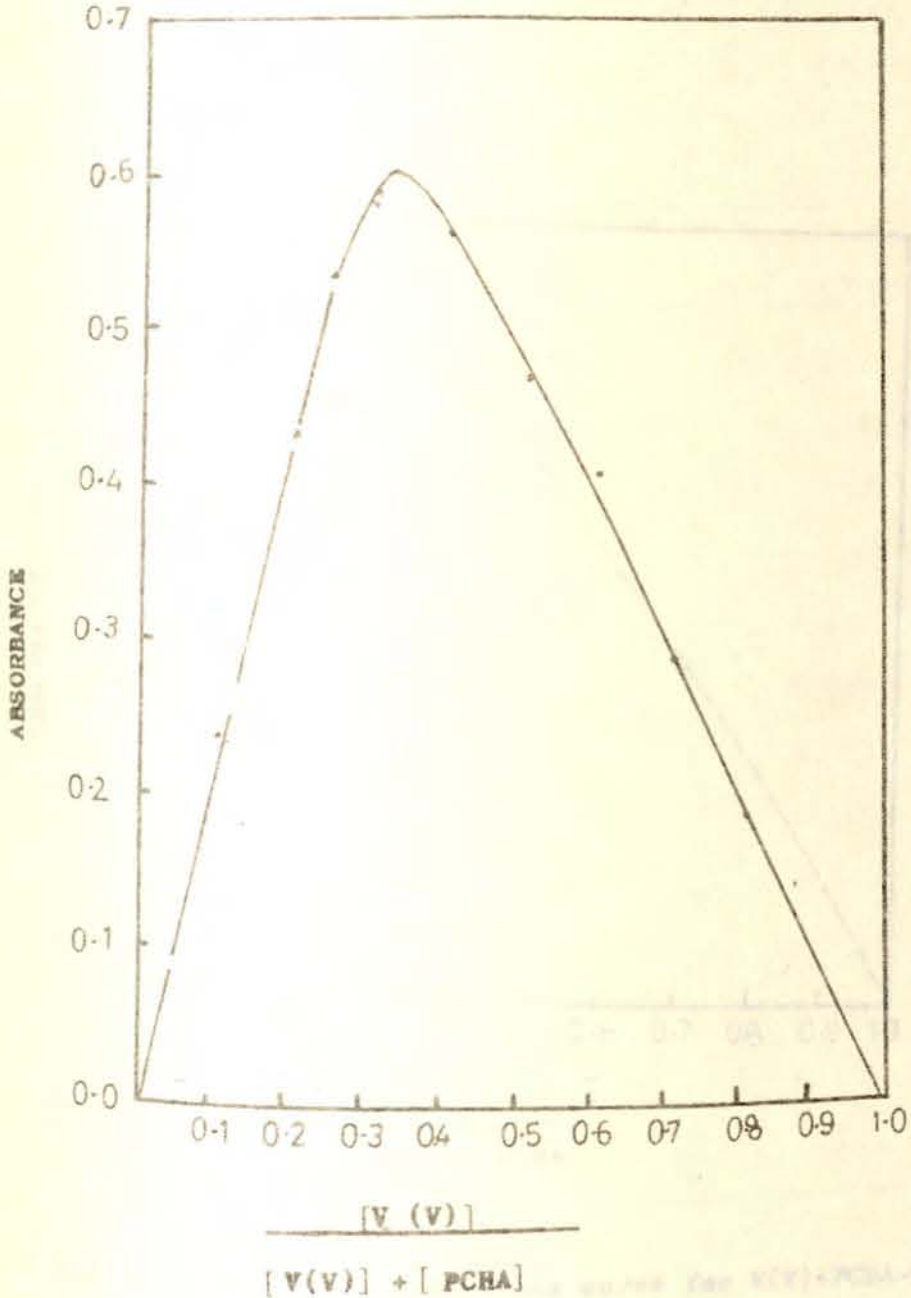


Fig. 12 Continuous variations curve for V(V)-PCHA-N_3 system.

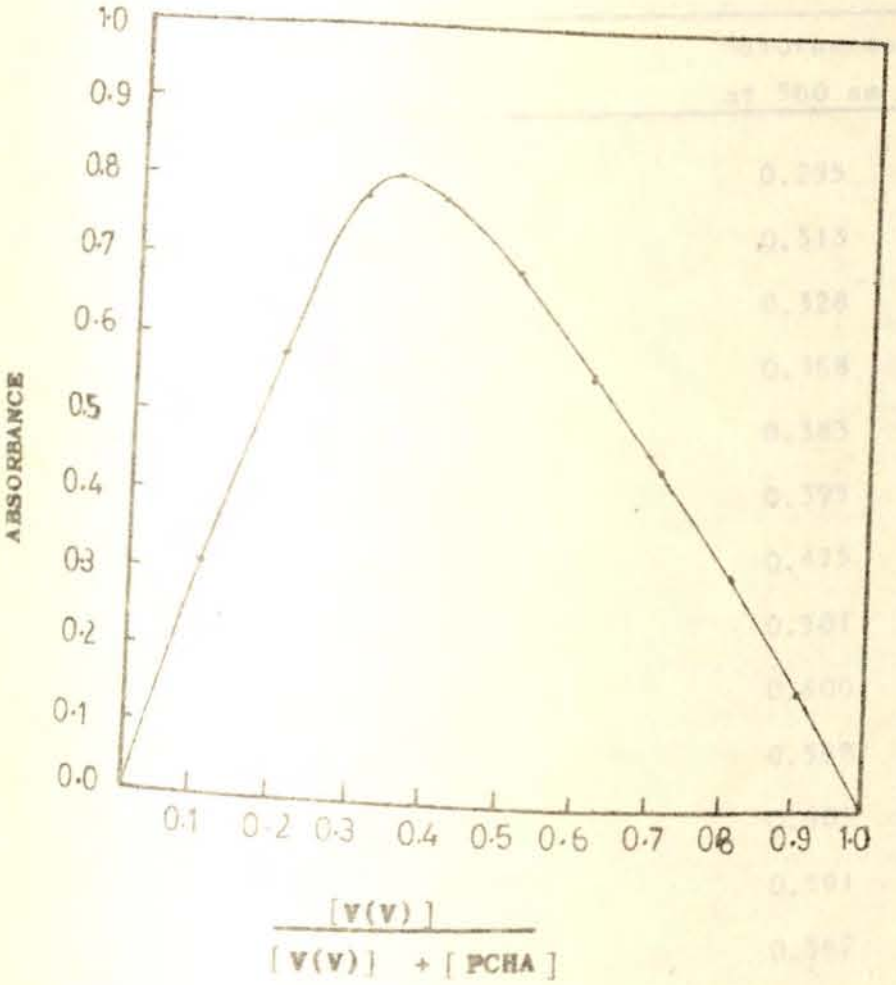


Fig. 13 Centinious variations curve for V(V)-PCHA-TCAA system

Table 9: Results of Simple Spectrophotometric Method for Determination of Composition of Vanadium Complex in V(V)-PCHA-N_3 System. $[V(V)] = 9.5 \times 10^{-5}$ M, $[HCl] = 0.1$ M, $[PCHA] = 2 \times 10^{-3}$ M

Concentration of Azide, M	Absorbance at 560 nm
0.00	0.295
0.005	0.313
0.01	0.328
0.03	0.368
0.04	0.383
0.05	0.395
0.075	0.475
0.10	0.501
0.20	0.600
0.50	0.598
1.00	0.601
1.50	0.591
2.00	0.562

Table 10. Results of Simple Spectrophotometric Method for Determination of Composition of Vanadium (V) Complex in V(V)-PCHA-TCAA System. $[V(V)] = 1 \times 10^{-4}$ M, $[PCHA] = 2 \times 10^{-3}$ M

Concentration of Trichloro-acetic Acid, M	Absorbance at 542 nm
0.00	0.311
0.01	0.383
0.02	0.420
0.04	0.459
0.06	0.485
0.10	0.523
2.00	0.618

Table 11. Data for Determination of Composition of Vanadium (V) Complex by Simple Spectrophotometric Method in V(V)-PCHA-N_3^- System. $A_{min} = 0.295$, $A_{max} = 0.60$

$\log [N_3^-]$	A	$A-A_{min}$	$A_{max}-A$	$\log \frac{A-A_{min}}{A_{max}-A}$
-2.30	0.313	0.018	0.287	-1.20
-2.0	0.328	0.033	0.272	-0.92
-1.52	0.368	0.073	0.232	-0.50
-1.4	0.383	0.088	0.217	-0.39
-1.3	0.395	0.1	0.205	-0.31
-1.12	0.475	0.18	0.125	0.158

Table 12. Data for Determination of Composition of Vanadium (V) Complex by Simple Spectrophotometric Method in V(V)-PCHA-TCAA system. A_{min} = 0.311, A_{max} = 0.618

log [TCAA]	A	$A-A_{min}$	$A_{max}-A$	$\log \frac{A-A_{min}}{A_{max}-A}$
-2	0.383	0.072	0.235	-0.51
-1.7	0.420	0.109	0.198	-0.26
-1.4	0.459	0.148	0.159	-0.031
-1.22	0.485	0.174	0.133	0.12
-1.0	0.523	0.212	0.095	0.35

A ratio of 1:1 (vanadium (V) to azide) in the mixed ligand complex was further supported by the absorption spectra studies. An identical spectra of the mexed ligand complex were found in the absence and presence of ethanol while different spectra were found for the simple complex in the absence and presence of ethanol. These results indicate the presence of an -OH group in the simple vanadium (V)-PCHA complex molecule and the absence of the -OH group in the mixed ligand V(V)-PCHA-N_3 complex molecule. This is possible only when the -OH group is being replaced by the $-N_3$ group during the mixed ligand complex formation. Since there is only one -OH group in the simple complex molecule only one $-N_3$ group can be co-ordinated with the metal which confirms the ratio of vanadium (V) to azide to be 1:1 in the mixed ligand complex. Such spectral study was not possible in the case of

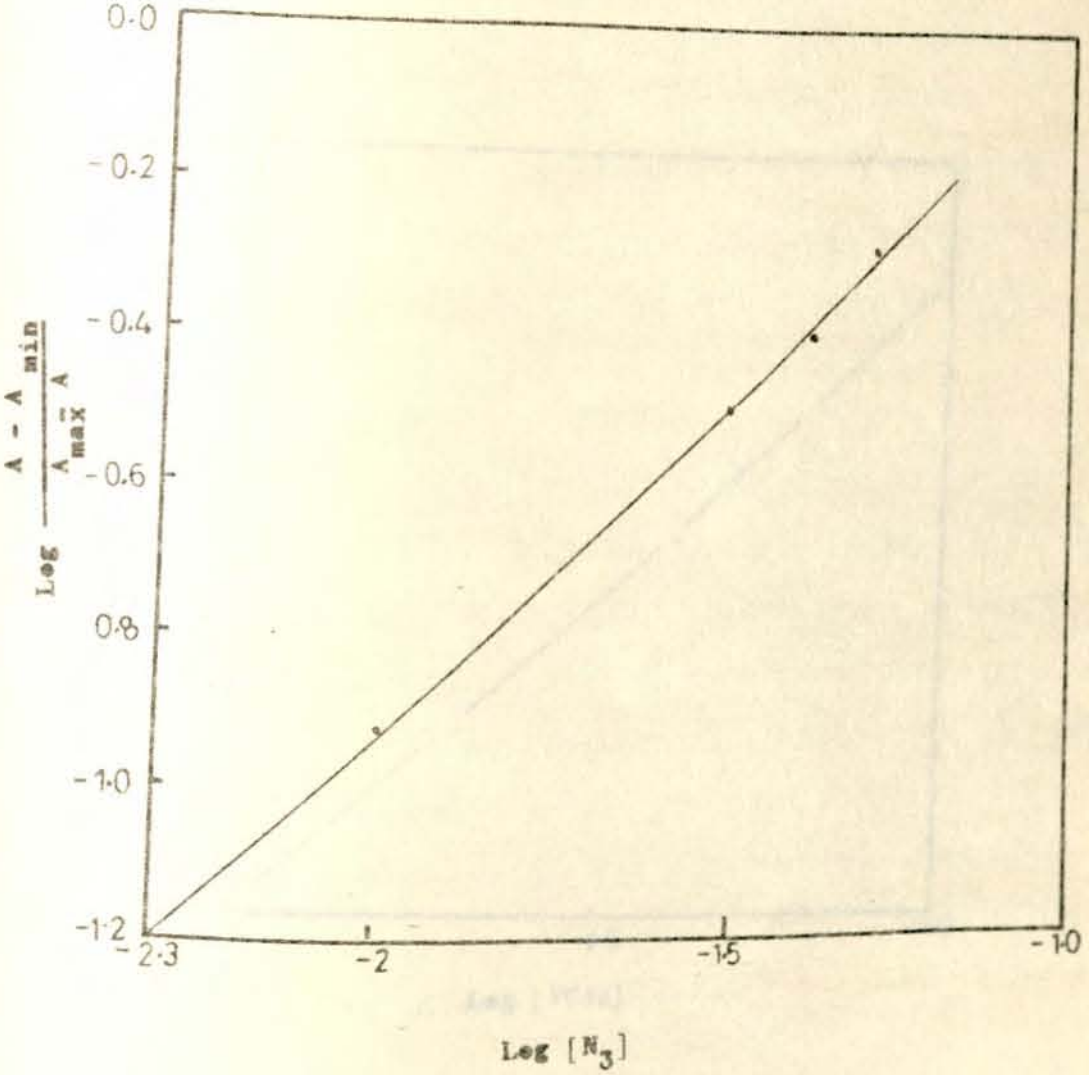


Fig. 14 Simple spectrophotometric method curve for V(V)-PCBA-N_3^- system.

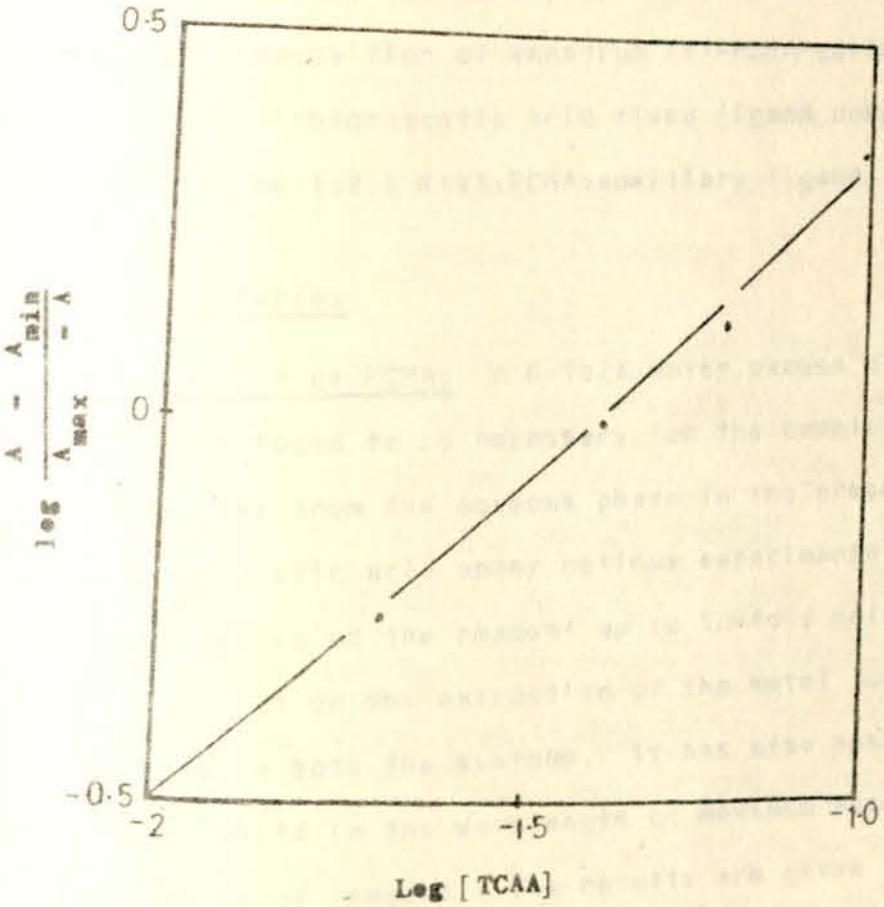


Fig. 15 Simple spectrophotometric method curve for V(V)-PCHA-TCAA system.

trichloroacetic acid since there was esterfication reaction between the carboxylic acid and the alcohol.

Thus the ratio of vanadium (V) to PCHA was found to be 1:2 by both the mole ratio and continuous variations methods in both systems and the ratio of vanadium (V) to azide and vanadium (V) to trichloroacetic acid to be 1:1 by simple spectrophotometric method and absorption spectra studies. Hence the overall composition of vanadium (V)-PCHA-azide and vanadium (V)-PCHA-trichloroacetic acid mixed ligand complexes have been found to be 1:2:1 (V(V):PCHA:auxiliary ligand).

3.3 Effect of Variables

Effect of Amount of PCHA: A 6-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 azide or trichloroacetic acid under optimum experimental conditions. A large excess of the reagent up to 50-fold molar excess has no adverse effect on the extraction of the metal ion from the aqueous phase in both the systems. It has also been found that there is no shift in the wavelength of maximum absorption with varying amount of reagent. The results are given in Table 5 and 6.

Effect of Concentration of Azide and Trichloroacetic Acid: The optimum concentration ranges of azide and trichloroacetic acid in the aqueous phase for complete extraction of vanadium (V)

were found to be 0.2 -1.0 M and 2-5 M respectively. At lower concentration of azide or trichloroacetic acid the formation of the mixed ligand complexes were incomplete. At higher concentration of azide water soluble azide-metal complex becomes more stable resulting in an incomplete extraction of vanadium (V). At higher concentration of trichloroacetic acid there was no phase separation. The results are given in Table 9 and 10.

Order of Addition of Reagents: It has been found that there is no change in the absorbance or in the color intensity of both the mixed ligand complexes extracted into chloroform if the order of addition of reagent is changed.

Ionic Strength, Temperature and Volume of Aqueous Phase: The wavelength of maximum absorption and absorbance value of colored extracts of both the complexes were not affected by the change in ionic strength of the aqueous phase between 0.5 M and 1.5 M with respect to potassium chloride or potassium nitrate. Variation in the temperature of both the systems between 10°C and 40°C did not produce any significant change in the absorbance values of the colored extracts of both the complexes. It has also been found that the volume of the aqueous phase can be varied from 10 to 100 ml in V(V)-PCHA-N_3 system and from 5 to 25 ml. in the V(V)-PCHA-TCAA system with respect to a fixed volume of 10 ml of the organic phase without any significant variation in the absorbance value or extraction efficiency of both the complexes. Further increase in volume of the aqueous phase in

V(V)-PCHA-TCAA system resulted in an incomplete extraction of vanadium (V) due to increasing miscibility of the two phases. The results are given in Tables 13-15.

Table 13. Effect of Ionic Strength in the Aqueous Phase on Extraction of Vanadium (V)

V(V)-PCHA-N_3^- System $[V(V)] = 1.06 \times 10^{-4}$ M $[N_3^-] = 0.5$ M, $[HCl] = 0.5$ M		V(V)-PCHA-TCAA System $[V(V)] = 1 \times 10^{-4}$ M [TCAA] = 3 M	
Concentration of KCl in aqueous phase, M	Absorbance at 560 nm	Concentration of KNO_3 in aqueous phase, M	Absorbance at 542 nm
0.5	0.675	0.5	0.778
1.0	0.672	1.0	0.770
1.5	0.676	1.5	0.774

Table 14. Effect of Temperature on Extraction of Vanadium (V)

V(V)-PCHA-N_3 System $[V(V)] = 1.06 \times 10^{-4}$ M $[N_3^-] = 0.5$ M, [HCl] = 0.5 M		V(V)-PCHA-TCAA System $[V(V)] = 1 \times 10^{-4}$ M [TCAA] = 3 M	
Temperature of the System, ^oC	Absorbance at 560 nm	Temperature of the System, ^oC	Absorbance at 542 nm
10	0.678	10	0.765
20	0.672	20	0.769
30	0.674	30	0.764
40	0.671	40	0.767

Extraction Time and Stability of Complexes: The vanadium (V)-PCHA-N_3 complex was completely extracted into chloroform within 3-4 minutes while the vanadium (V)-PCHA-TCAA complex was completely extracted into chloroform within two minutes. It has also been found that the maximum color intensity, i.e. the constant absorbance of the chloroform extract of the V(V)-PCHA-N_3 complex was attained within 2 hours of standing time and the a absorbance value of the complex remained constant at least for 2 days at 20 ± 2^oC. The chloroform extract of the vanadium (V)-PCHA-TCAA was stable for at least 3 days at 20 ± 2^oC from the time of its extraction. These results are also true if one uses chloroacetic acid instead of trichloroacetic acid. The results are given in Table 16.

Table 15. Effect of Volume of Aqueous Phase on Extraction of Vanadium (V)

V(V)-PCHA-N_3^- System		V(V)-PCHA-TCAA System	
$[V(V)] = 1.06 \times 10^{-4}$ M,		$[V(V)] = 1 \times 10^{-4}$ M,	
$[N_3^-] = 0.5$ M		[TCAA] = 3 M, V_{org} = 10 ml	
[HCl] = 0.5 M, V_{org} = 10 ml			
Aqueous Phase Volume, ml	Absorbance at 560 nm	Aqueous Phase Volume, ml	Absorbance at 542 nm
10	0.670	5	0.768
25	0.673	10	0.770
50	0.669	25	0.765
100	0.674	-	-

Table 16. Effect of Time on Absorbance of Vanadium (V) Complexes

Complex System	V (V)-PCHA-N_3^- [V(V)] = 1.23×10^{-4} M, $[N_3^-]$ = 0.5 M, [HCl] = 0.5 M	V(V)-PCHA-TCAA [V(V)] = 1×10^{-4} M, [TCAA] = 3 M	V(V)-PCHA-CAA [V(V)] = 1×10^{-4} M, [CAA] = 5 M
Time min/hr/day	Absorbance of Chloroform Extract at 560 nm	Absorbance of Chloroform Extract at 542 nm	Absorbance of Chloroform Extract at 530 nm
0	0.728	0.775	0.665
30 min	0.744	0.775	0.668
1 hr	0.750	0.774	0.662
2 hrs	0.768	0.775	0.664
3 hrs	0.766	0.773	0.665
12 hrs	0.766	0.774	0.663
24 hrs	0.770	0.775	0.667
32 hrs	0.768	0.774	0.662
36 hrs	0.767	0.775	0.661
2 days	0.769	0.774	0.662
3 days	decomposed	0.770	0.660

3.4 Spectral and Photometric Characterstics of Complexes

The molar absorptivity and photometric sensitivity (6) of the mixed ligand complexes have been determined at the long wavelengths of maximum absorption where the reagent, PCHA, has negligble absorbance. The results are summarized in Table 17.

Table 17. Molar Absorptivity and Sensitivity of the Colored Systems

Complex System	λ_{max} nm	ε_{max} l mole^{-1} cm^{-1}	Photometric Sensitivity µg V cm^{-2}
V-PCHA-N_3	560	6300	0.0080
V-PCHA-TCAA	542	7750	0.0066
V-PCHA-CAA	530	6680	0.0076

The colored systems obeyed Beer's law in the concentration range of 0.9 - 10 ppm, 0.6 - 8 ppm, and 0.8 - 10 ppm of vanadium in the V(V)-PCHA-N_3, V(V)-PCHA-TCAA, V(V)-PCHA-CAA colored systems respectively. The results are given in Table 18-20 and the curves are shown in Fig. 16-18. The optimum concentration ranges for the determination of vanadium (V) as evaluated from Ringbom's plot (82) (Fig. 12-21) were found to be 1.8 - 8.5 ppm, 0.8-5.0 ppm and 1.2-7.0 ppm of vanadium for the V(V)-PCHA-N_3, V(V)-PCHA-TCAA, and V(V)-PCHA-CAA colored systems, respectively. These results indicate that the methods are highly sensitive and hence applicable to the determination of traces of vanadium.

Table 18. Calibration Curve Data for Determination of V(V) by V(V)-PCHA-N_3 System

Concentration of Vanadium (V)			Absorbance at 560 nm
M	µg/25 ml	ppm	
1.8×10^{-5}	22.73	0.92	0.116
2×10^{-5}	25.48	1.02	0.129
4×10^{-5}	50.95	2.04	0.260
8×10^{-5}	101.90	4.08	0.519
12×10^{-5}	152.85	6.12	0.771
16×10^{-5}	203.8	8.16	1.046
20×10^{-5}	254.75	10.2	1.270

Table 19. Calibration Curve Data for Determination of V(V) by V(V)-PCHA-TCAA System

Concentration of Vanadium (V)			Absorbance at 542 nm
M	µg/25 ml	ppm	
1.2×10^{-5}	15.28	0.61	0.092
2×10^{-5}	25.48	1.02	0.150
4×10^{-5}	50.95	2.04	0.310
8×10^{-5}	101.90	4.08	0.622
10×10^{-5}	127.4	5.10	0.775
12×10^{-5}	152.85	6.12	0.923
16×10^{-5}	203.8	8.16	1.20

Table 20. Calibration Curve Data for Determination of V(V) by V(V)-PCHA-CAA System

Concentration of Vanadium (V)			Absorbance
M	ug/25 ml	ppm	at 530 nm
1.6×10^{-5}	20.38	0.82	0.108
2×10^{-5}	25.48	1.02	0.135
4×10^{-5}	50.95	2.04	0.286
10×10^{-5}	127.4	5.1	0.670
20×10^{-5}	254.75	10.2	1.32

3.5 Precision

The precisions of the newly developed methods were evaluated by performing ten, five, and ten independent analyses on samples each containing 5.4, 4.08, and 5.10 ppm of vanadium in the V(V)-PCHA-N_3, V(V)-PCHA-TCAA and V(V)-PCHA-CAA systems, respectively. The results obtained (Table 21) clearly indicate that the methods are highly precise and give reproducible results.

Table 21. Evaluation of Precision of Methods

Parameter	Method based on V(V)-PCHA-N_3 system	Method based on V(V)-PCHA-TCAA system	Method based on V(V)-PCHA-CAA system
Total number of samples	10	5	10
V(V) concentration, ppm	5.40	4.08	5.10
Average deviation from mean, ppm	5.40±0.01	4.08±0.01	5.10±0.01
Relative standard deviation	0.67%	0.58%	0.50%

3.6 Effect of Foreign Ions

In order to evaluate the selectivity of the two newly developed methods the effect of several diverse ions on the extraction and determination of vanadium (V) with PCHA in the presence of azide or trichloroacetic acid has been investigated. The tolerance limit taken as the concentration (ppm) of ions which cause an error less than 2% are given in Table 22.

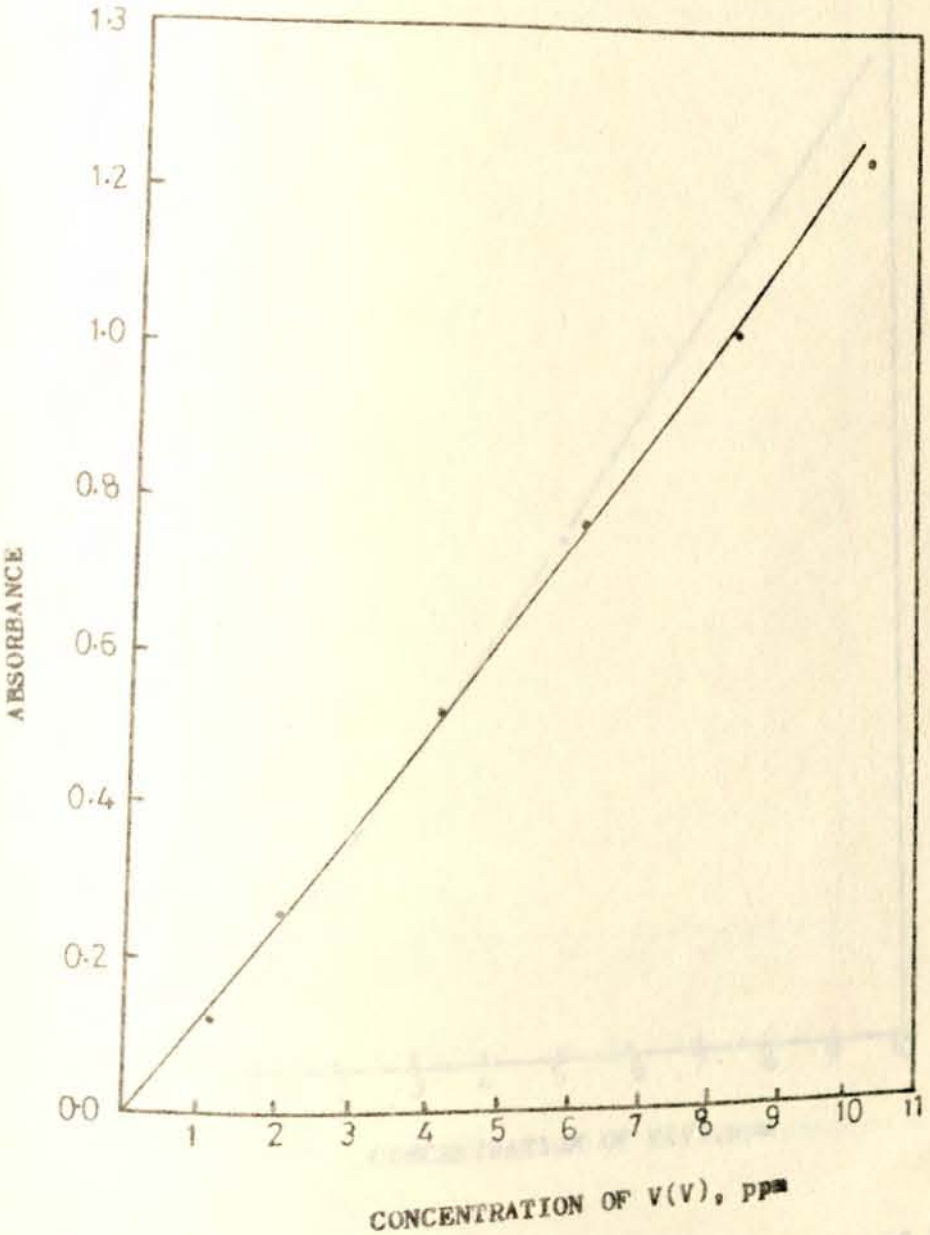


Fig. 16 Calibration curve for the determination of V(V) by V(V)-PCHA-N_3 system.

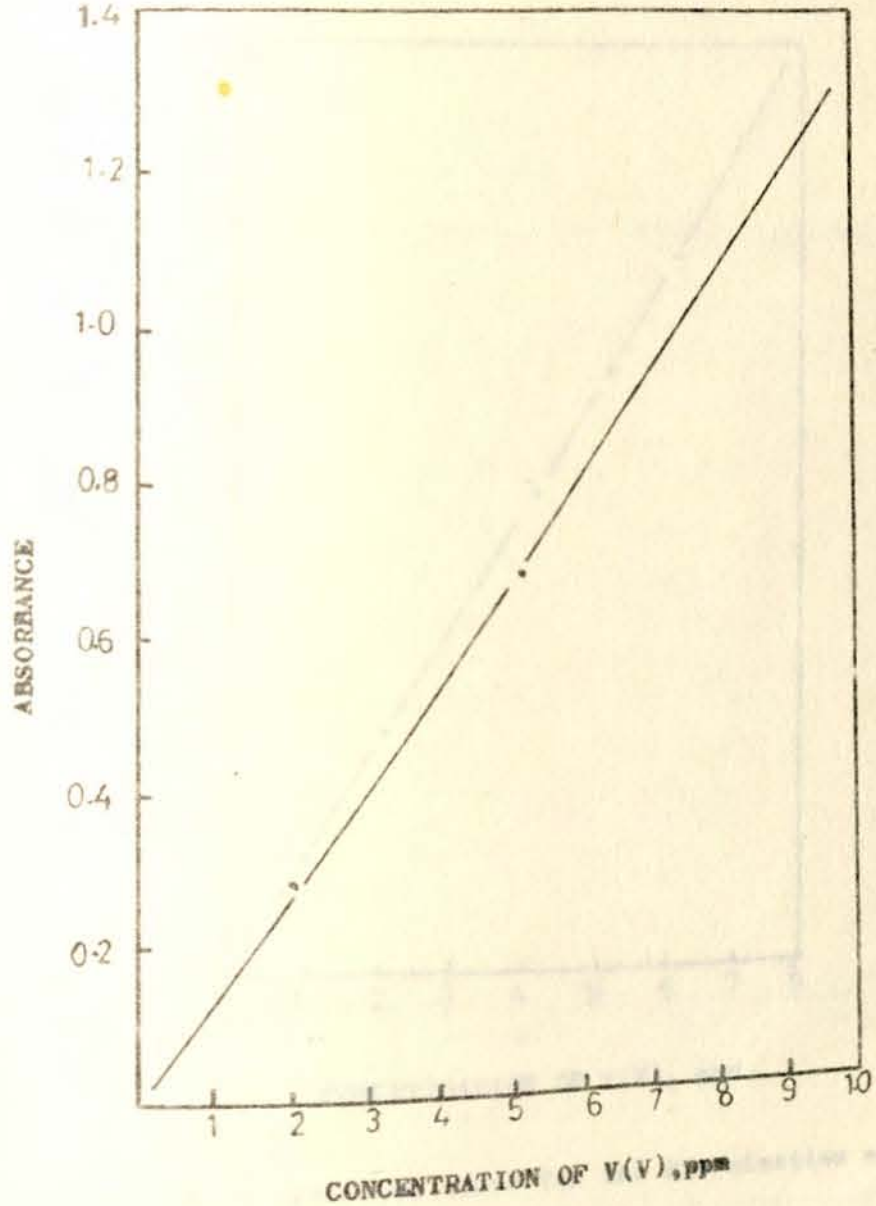


Fig. 17 Calibration curve for the determination of V(V) in V(V)-PCHA-CAA system.

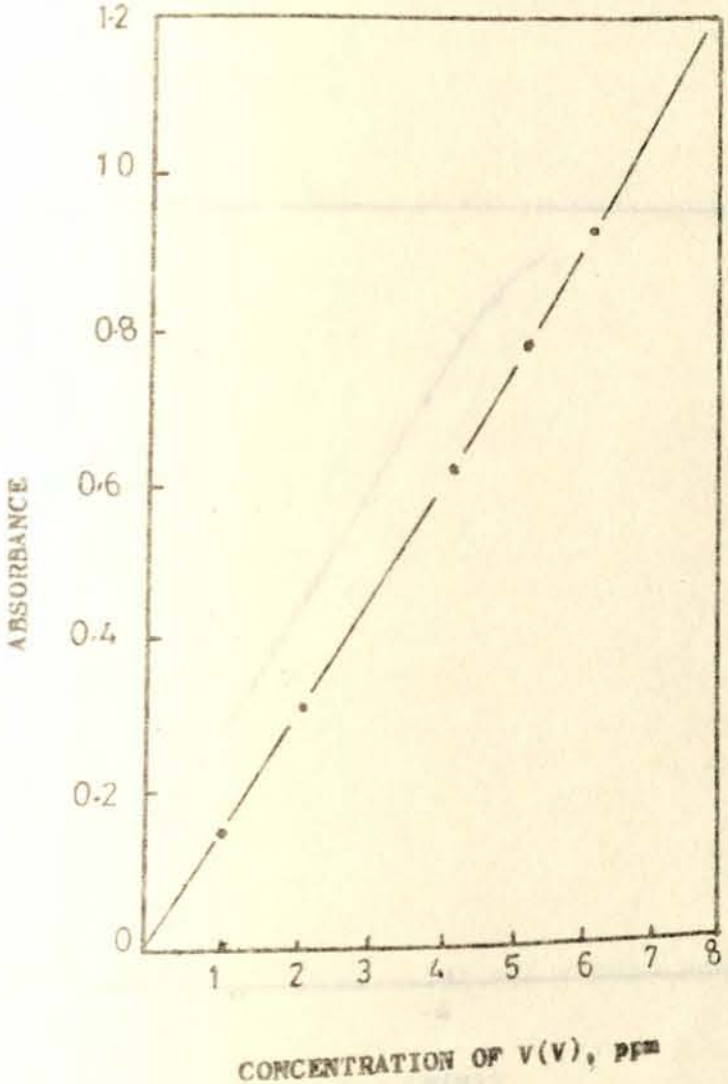


Fig. 18 Calibration curve for the dtermination of V(V) by V(V)-PCHA-TCAA system.

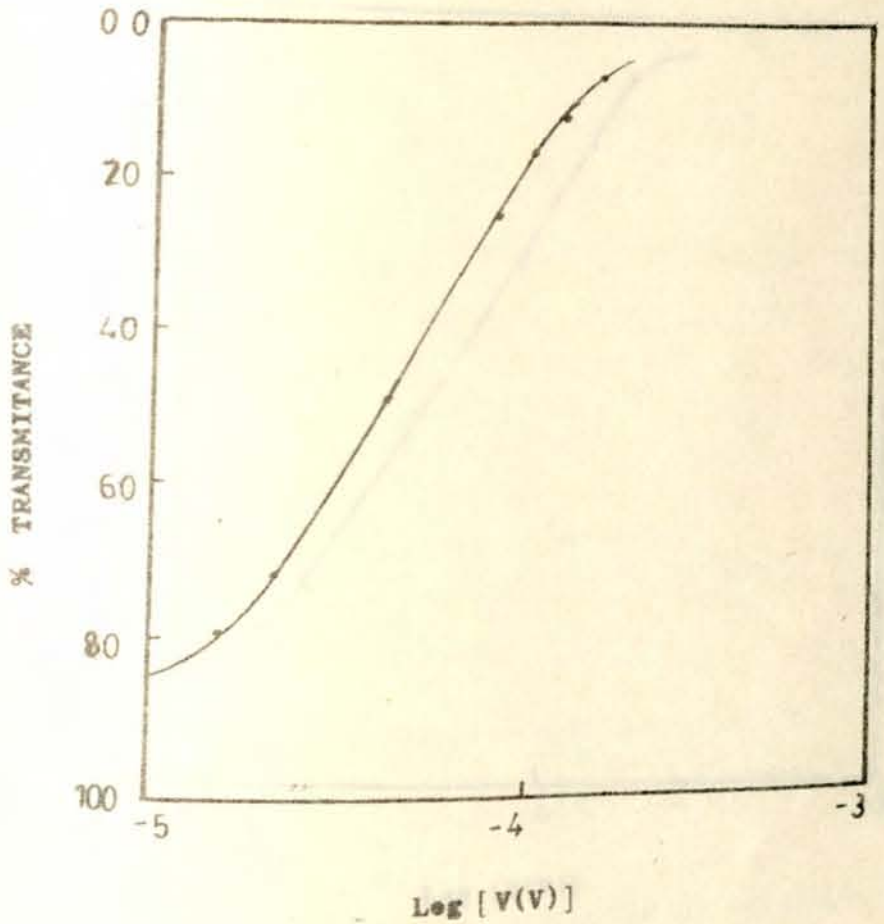


Fig. 19 Ringbom's plot to determine the effective concentration of V(V) by V(V)-PCHA-N_3 system.

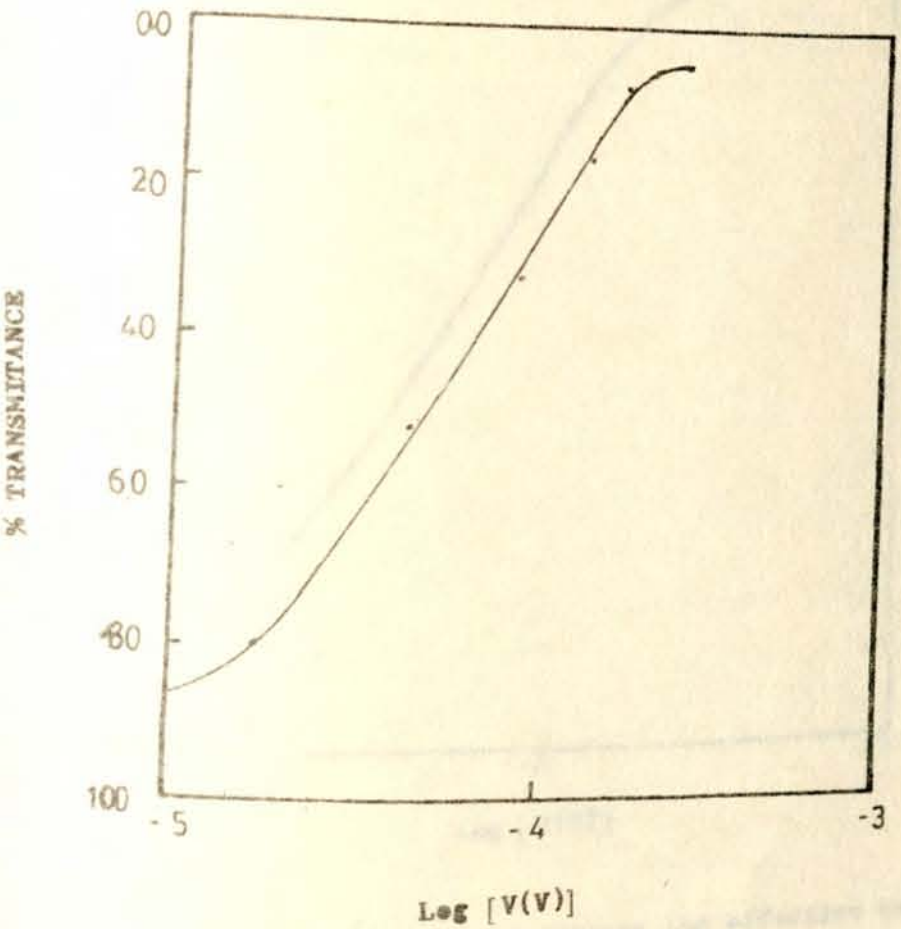


Fig. 20 Ringbom's plot to determine the effective concentrat
of V(V) by V(V)-PCHA-TCAA system

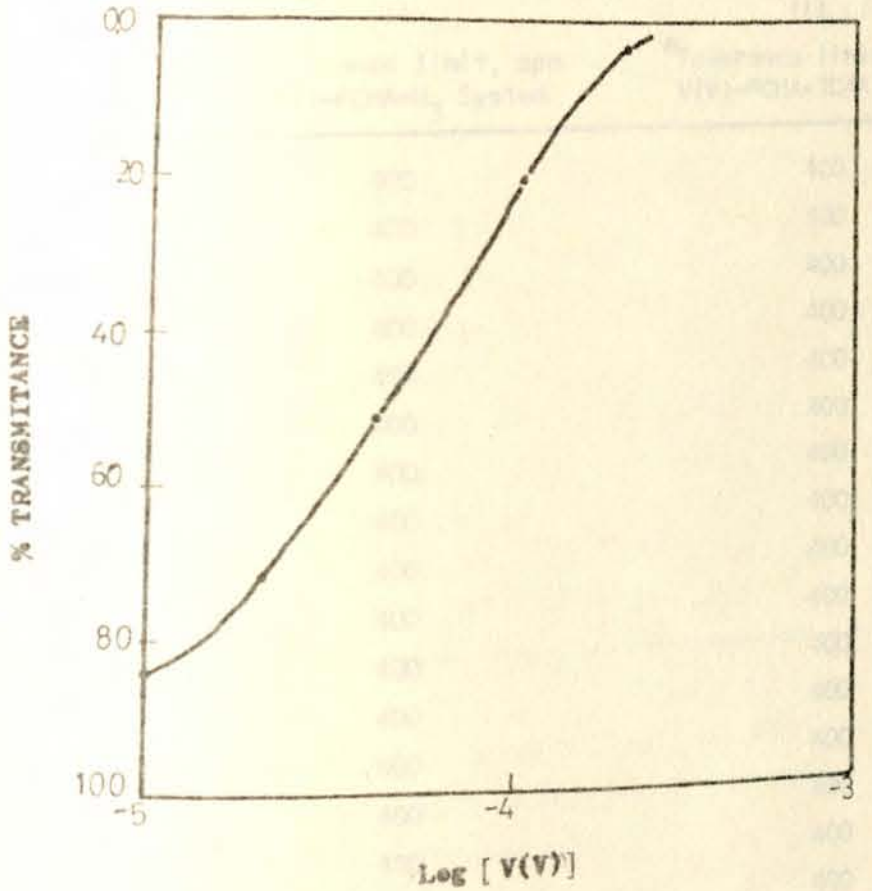


Fig. 21 Ringbem's plot to determine the effective concentration of V(V) by V(V)-PCHA-CAA system.

Table 22. Influence of Foreign Ions in the Determination of Vanadium (V) in V(V)-PCHA-N_3^- and (V(V)-PCHA-TCAA Systems. V(V) = 4 ppm, N_3^- = 0.5 M, TCAA = 3 M HCl = 0.5 M (for V(V)-PCHA-N_3^- System)

I Ion	II [a]Tolerance limit, ppm V(V)-PCHA-N_3^- System	III [a]Tolerance limit, ppm V(V)-PCHA-TCAA System
Na^+	400	400
K^+	400	400
Li^+	400	400
Ca^{2+}	400	400
Sr^{2+}	400	400
Ba^{2+}	400	400
Mg^{2+}	400	400
Be^{2+}	400	400
Al^{3+}	400	400
La^{3+}	400	400
Tl^+	400	400
Zn^{2+}	400	400
Cd^{2+}	400	400
Hg^{2+}	400	400
Sn^{4+}	400	400
Pb^{2+}	400	400
Bi^{3+}	400	200
Ce^{4+}	400	400
Th^{4+}	200	100
UO_2^{2+}	200	400
Cu^{2+}	100	300[b]
Fe^{3+}	400[b]	400
Ni^{2+}	400	400
Co^{2+}	400	400
Cr^{3+}	300	

I	II	III
Mn^{2+}	400	400
MoO_4^{2-}	80	40
WO_4^{2-}	100	80
Ti^{4+}	40	80[b]
Zr^{4+}	400	380
NH_4^+	400	400
Acetate	400	400
Chloride	400	400
Nitrate	400	400
Sulphate	400	400
Citrate	400	400
Tartarate	400	400
Phosphate	400	400
Borate	400	400
Fluoride	2400	3600
Oxalate	400	400
EDTA	150	400

[a]For most of the ions the tolerance limit might be well above 400 ppm. However, the exact limits were not determined since they did not interfer up to 400 ppm.

[b]Masked with Fluoride.

Iron (III) react with the reagents to form colored complex extractable into chloroform and interfere in the determination of vanadium (V) in V(V)-PCHA-N_3 system. The interference of iron (III) was eliminated by masking it with fluoride. A solution containing 10 mg/ml of fluoride was added portion-wise and shaked vigorously until the colored iron (III) azide complex

turned colorless. The lower tolerance limit of titanium((IV) can also be improved using fluoride as a masking agent. In V(V)-PCHA-TCAA system iron (III) and titanium (IV) interfere in the determination of vanadium (V). Again the interference of iron (III) and titanium.(IV) was eliminated by masking these ions with fluoride. A solution containing 0.2 gm/25 ml of NaF was added, to the solution containing iron (III) (7.5 mg) and titanium (IV) (2 mg) and shaked vigorously. Then V(V) was extracted and determined by the general procedure.

The results given in Table 22 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 and azide or trichloroacetic acid. Hence, the two newly developed methods are highly selective and can be applied for the determination of vanadium (V) in any type of samples.

3.7 Comparison of Common Spectrophotometric Methods for Determination of Vanadium.(V)

The comparison of the present methods with the common spectrophotometric methods with common spectrophotometric methods used for the determination of vanadium is summarized in Table 23. The newly developed methods are selective since most of the common ions including Fe (III), Ti (IV), Zr (IV), and Mo (VI) do not interfer. The sensitivity of the methods is good and the methods are free from the rigid control of experimental conditions.

is good and the methods are free from the rigid control of experimental conditions.

Table 23. Comparison of Common Spectrophotometric Methods

I Reagent	II λ_{max} nm	III Sensitivity $\mu g\ V\ cm^{-2}$	IV Optimum Acidity Range	V Interference	VI Reference
Hydrogenperoxide	450	varies with acidity	0.6-6 N	Fe, Cr, Mo, Ti, W	83
Phosphofungstic acid	400	0.027	0.5 M	Fe,Cr,Cu, Co,Mo,Sn, Sb, Ti	84
Tropolone	590	0.011	5.5-7 M HCl	Mn, Br, I	85
3-Hydroxyl-1, 3-diphenyltrazine	410	0.0078	3.0-6.0 pH	Fe,Cr,Cu, Mn, Co	86
1-(2-pyridycazo)-2-napthol	615	0.003	3.5-4.5 pH	Fe,Cr,Cu, Mn, Co	87
8-Hydroxyquinoline	550	0.016	3.5-45 pH	Fe,Cu,Mn	88
8-Hydroxyquinoline in presence of p-phenyl phenol	620	0.008	2.5-5.0 pH	*	84
Benzo-hydroxamic acid	450	0.014	1.2-5.5 pH	Fe,Mn,Al	89,90

I	II	III	IV	V	VI
N-phenylbenzo-hydroxamic acid	530	0.011	5.0-9.0 M HCl	Ti,Zr, Mo, W	53
N-phenylcinnamo-hydroxamic acid	540	0.008	3.0-7.5 M HCl	Ti,Zr, Mo, W	39
N-phenylcinnamo-hydroxamic acid in presence of P-chlorophenol	565	0.0068	1.0-3.0 M	W	46
N-phenylcinnamo-hydroxamic acid in in presence of thiocyanate	590	0.0068	3.0-7.0 M HAC	Fe, W	45
N-phenylcinnamo-hydroxamic acid in presence of azide	560	0.0080	0.03-1.5 M HCl	*	-
N-phenylcinnamo-hydroxamic acid in presence of trichloroacetic acid	542	0.0066	2.0-5.0 TCAA	*	-

*Interference of iron is eliminated by masking.

3.8 Applications of the Methods

The newly developed methods were applied for the determination of vanadium in blood and steel samples to asses their analytical potentiality.

Steel Samples: Since the standard samples were not available, synthetic samples having the same composition as that of the British Chemical Standard Steel No. 64a and 241/1 were prepared. Extraction and determination of the samples were undertaken following the general procedure described earlier. The results are given in Table 24.

Table 24. Determination of Vanadium (V) in Synthetic Steel Samples

Method	Sample No.	Vanadium Content (%)	*Vanadium Found (%)	R.S.D. (%)
V-PCHA-N_3	64a	1.57	1.54	0.81
			1.55	0.74
	241/1	1.57	1.55	0.76
			1.56	0.68
V-PCHA-TCAA	64a	1.57		
	241/1	1.57		

*Average of 3 determinations.

Composition of Samples

Sample No. 64a: C, 0.80; Cr, 4.40; V, 1.57; Mo, 4.11; W, 5.66; Fe, 83.45%

Sample No. 241/1: W, 19.61; Cr, 5.03; Mo, 0.52; V, 1.57; Co, 5.67; C, 0.85; Si, 0.33; S, 0.033; P, 0.02; Mn, 0.295; Ni, 0.075; Cu, 0.1; Sn, 0.025; Fe, 65.87%.

Blood Sample: It has been found from the analysis that the blood sample from an adult person did not contain any detectable amount of vanadium. This has been shown by adding a known amount of vanadium to the blood before the sample preparation as described earlier. The vanadium content of the sample solution was determined by the V(V)-PCHA-TCAA (or CAA) method. The results are given in Table 25.

Table 25. Determination of Vanadium after standard Addition to Blood Sample

Method	Vanadium Added	*Vanadium Found	R.S.D.(%)
V-PCHA-TCAA	0.10 mg	0.0995	0.58
V-PCHA-CAA	0.10 mg	0.0990	0.60

*Average of 3 determinations.

The results given in Tables 24 and 25 indicate that the newly developed methods are reliable and can be applied to the analysis of vanadium (V) in a variety of samples.

4. CONCLUSION

Two new simple, rapid, and reliable methods for the extraction and spectrophotometric determination of vanadium (V) with N-phenylcinnamohydroxamic acid and azide or trichloroacetic acid have been developed. Both the newly developed methods are sensitive, selective, and give reproducible results. Moreover, as the methods are largely free from the rigid control of the experimental variables they can have wide analytical applicability for the successful determination of vanadium in bio-samples, alloys, rocks, soils, etc. The disadvantage of the methods is the additional steps taken for masking of interfering ions.

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D E C L A R A T I O N

I, the undersigned, declare that this thesis is my work and that all sources of material used for the thesis have been duly acknowledged.

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