TO Woizero Zewditu Adankew, my grandmother

and

Sebsebe Demissew, a real friend

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

PAGE

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

N-PHENYLCINNAMOHYDROXAMIC ACID AS AN ANALYTICAL REAGENT FOR SOLVENT EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM (V)

by

Mulugeta Assefa

Research advisor: B.S. Chandravanshi

N-phenylcinnamohydroxamic acid (PCHA) has been found to form a convenient extraction system for uanadium (V) in presence of p-chlorophenol and also in SCN media. PCHA reacts with vanadium (V) to give a 1:2 complex (having a broad peak around 540 nm with 6200 litres/mole/cm). In the presence of an adduct forming substance (p-chlorophenol) synergic extraction of the metal and marked absorbance enhancement into chloroform have been observed on the basis of formation and hyper and bathochromic shift of the hydrophobic species formed. Similar effect is seen in the mixed ligand complex system. The complexes are found to have the composition 1:2:1 or 1:2:2 (V: PCHA: PhOH) depending upon the amount of p-chlorophenol available during the reaction; and 1:2;2 (V: PCHA: SCN) mixed

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complex. The effective molar absorbance and the photometric sensitivity being 7500l/mole/cm and 0.0068µg of vanadium per cm^2 respectively in both systems. Most of the common ions usually associated with vanadium in alloys and complex materials do not interfere. The influence of several experimental variables have been studied and the synergic extraction system has been successfully applied for the determination of vanadium in synthetic composite steel samples. On the basis of these studies new methods for the extraction and spectrophotometric determination of vanadium (V) have been developed.

I. INTRODUCTION

Organic reagents are widely used in inorganic analysis because of the inherent selectivity, sensitivity and specificity of their reaction with metal ions (1 - 9). Recent advances in chemical technology has shown that the presence of traces of less familiar elements in alloys and complex materials modify the properties significantly. And hence, there is an increasing awareness for developing methods of detection and estimation of various elements present in traces. New more selective and sensitive reagents are being sought after and applied for such analyses. Wide potentialities for the discovery of highly sensitive and selective reagents are offered to analytical chemists by the large number of available compounds. There is a great possibility of modifying the sensitivity and selectivity of the analytical methods by the introduction of auxilary reagents through the formation of adducts and mixed ligand complexes and to develop new methods.

Organic reagents, on the basis of their reactions with metal ions have been broadly classified as:

(i) normal salt forming type,
(ii) reagent forming adsorption compounds,

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(iii) uncharged organic molecules forming metal chelates,

(iv) reagents forming uncharged metal chelates (inner complexes).

The most important organic reagents are those forming chelate complexes (inner complexes) in which the metal ions are bound to the ligand via at least two donor atoms and the ligand must possess at least one acid group with a replaceable hydrogen atom and a basic, co-ordinating donor group. For analytical applications, the most suitable reagents are usually those compounds in which the acid and basic groups are in such a position as to form five-or six-membered chelate rings which are most stable.

The chemical and physical properties of a metal chelate depends upon the basic nature of chelating agent and the acidic nature of the metal as well as on factors inherent in the complex itself.

There are some striking properties of chelates which have proved to be most useful in the determination of metals. For example, some metal chelates are sufficiently insoluble in a given solvent and can be used for gravimetric determination of metal ions. Some of the complexes produce fluorescence in solution

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and find extensive application in fluorimetric analysis. Many of the inner complexes are intensely coloured to enable the spectrophotometric determination of metal ions. Further, extraction of a coloured reaction products into an immiscible organic solvents is very often used to increase the sensitivity and renders the reaction of the reagent more selective. The extraction of certain metal complexes which do not have all their co-ordination sites saturated by the chelating reagent, can be increased by the addition of secondary complexing agent either due to the formation of mixed complexes or due to synergic extraction.

Frequently sufficient selectivity and sensitivity can be achieved for a particular purpose by controlling the reaction conditions and also by taking advantage of masking agents.

1.1 SOLVENT EXTRACTION

Solvent extraction is probably the most versatile of all analytical techniques. It has come to be recognized as a popular separation technique because of the elegance, simplicity, speed and application to both tracer and macro amounts of metal ions. It frequently appears to be the ideal method for separating trace constituent from large amounts of other substances. The process is often very selective and the isolation of the metal in question can usually be made as complete as possible. A significant trend in solvent extraction is simultaneous extraction and determination of any species in the organic phase. In many cases the process has become a method of choice for 'determination' rather than merely of 'separation'. The extraction of the coloured metal complex from one solvent (usually water) into another (generally an organic solvent) often permit a considerable concentration of the complex to be achieved with a consequent increase in the sensitivity of the procedure involved. The most common methods of determination are the spectrophotometric methods. It is also possible to take advantage of the volatility of the substance isolated in the organic phase in gas chromatography or if the extracted substance can be readily decomposed into a flame, it can be determined by flamephotometry or by atomic absorption spectroscopy. In some cases, the solute may be recovered quantitatively by evaporating the solvent or back extraction into an aqueous phase by the addition of an oxidizing, reducing or specific complexing substances or by change of pH.

Solvent extraction is quite a universal method and is widely used in analytical chemistry, extraction procedures have been reported for the majority of elements in the literature (10 - 14). By using solvent extraction, important theoretical problems concerning the composition and stability of soluble as well as insoluble metal complexes can be solved. They are also being used in spot test analysis by accumulation of a reaction product at the interface of two immiscible liquids. The extraction is generally represented in terms of distribution ration 'D' (or extraction coefficient 'E') defined as:

$$D = \frac{\text{Total concentration in the organic phase}}{\text{Total concentration in the aqueous phase}}$$

Generally compounds which are only slightly soluble in water but readily soluble in organic solvents can usefully be extracted because the partition coefficient of a compound is approximately equal to the ratio of its solubilities in the organic and aqueous phase.

Organic reagents play an eminent role in solvent extraction, because they can react with metal ions to give products having the basic prerequisite for extractability. These products are electrically neutral, essentially covalent chelate compounds which are only slightly soluble in water but readily soluble in organic solvents.

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One of the most powerful group of organic reagents used for solvent extraction and spectrophotometric analysis in recent years is N-arylhydroxamic acids which forms the basis of this thesis. The general properties and analytical applications of N-arylhydroxamic acids are reported (26 - 33).

1.2. N-ARYLHYDROXAMIC ACIDS AS REAGENTS FOR SOLVENT EXTRACTION AND SPECTROPHOTOMETRY

N-Arylhydroxamic acids are widely used for the solvent extraction and spectrophotometric determination of metal ions. The sensitivity and selectivity of an analytical reagent can be modified either by changing the substituent groups attached to the functional grouping or by changing the reaction medium and introducing an auxiliary complexing agent forming adduct or mixed complexes. Thus by changing the reaction medium of hydroxamic acids and introducing auxiliary reagents it has been possible to develop new methods with better sensitivity and selectivity for the extraction and spectrophotometric determination of metal ions. Hence, the study of effects of phenols and thiocyanate ion on the extraction and spectrophotometric

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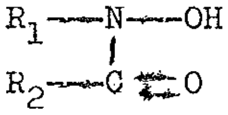
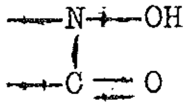
determination of vanadium (V) with N-Phenylcinnamohydroxamic acid was undertaken and their analytical applications were explored.

N-Arylhydroxamic acids represented by the general formula, I, are monobasic and bidentale chelating agents having the reactive functional grouping, II, which is capable of forming a five-membered ring on chelation with metal ions. They are stable towards heat, light and air and can be stored indefinitely. These are crystalline solids, slightly soluble in water but readily soluble in organic solvents. Their solutions in organic solvent are colourless and stable for several days which is a desirable characteristic for the spectrophotometric reagents.



$$\begin{array}{l} R_1-N-OH \\ \qquad\; | \\ R_2-C=O \end{array}$$

I



$$\begin{array}{l} -N-OH \\ \quad | \\ -C=O \end{array}$$

II

The metal chelates of N-aryhydroxamic acids are water insoluble, thermally stable, of definite composition and directly weighable. These excellent properties of the metal complexes have led to development of gravimetric methods for the determination of metal ions. Most of the metal chelates are readily

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extracted into various organic solvents from the aqueous phase thus forming the basis of solvent extraction procedure. The coloured chelates have been used for the spectrophotometric determination of several metal ions by solvent extraction. They also find extensive applications in spot tests, as indicators and as masking agents in analysis.

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II. LITERATURE SURVEY

The literature of the last 30 years abounds in many diverse studies and analytical applications of N-arylhydroxamic acids and their metal complexes. They are now so well recognized as reagents, that their analytical applications are described in considerable details in reviews, monographs, treaties and textbooks (3,4,10-12, 15-19). Most of the diverse applications of hydroxamic acids have been described in detail by Majumdar (18).

One of the most important reagents in the family of hydroxamic acids is N-phenylcinnamohydroxamic acid, PCHA, III, which is selected for the present studies. It was first introduced as a chelating agent for the extraction and spectrophotometric determination of vanadium (V) by Tandon (20). Its use was later extended for the extraction and spectrophotometric determination of iron (III), hafnium (IV), niobium (V), titanium (IV), uranium (VI) and zirconium (IV) (21 - 23). And for the gravimetric determination of niobium (V), tantalum (V) and zirconium (IV) (24,25).

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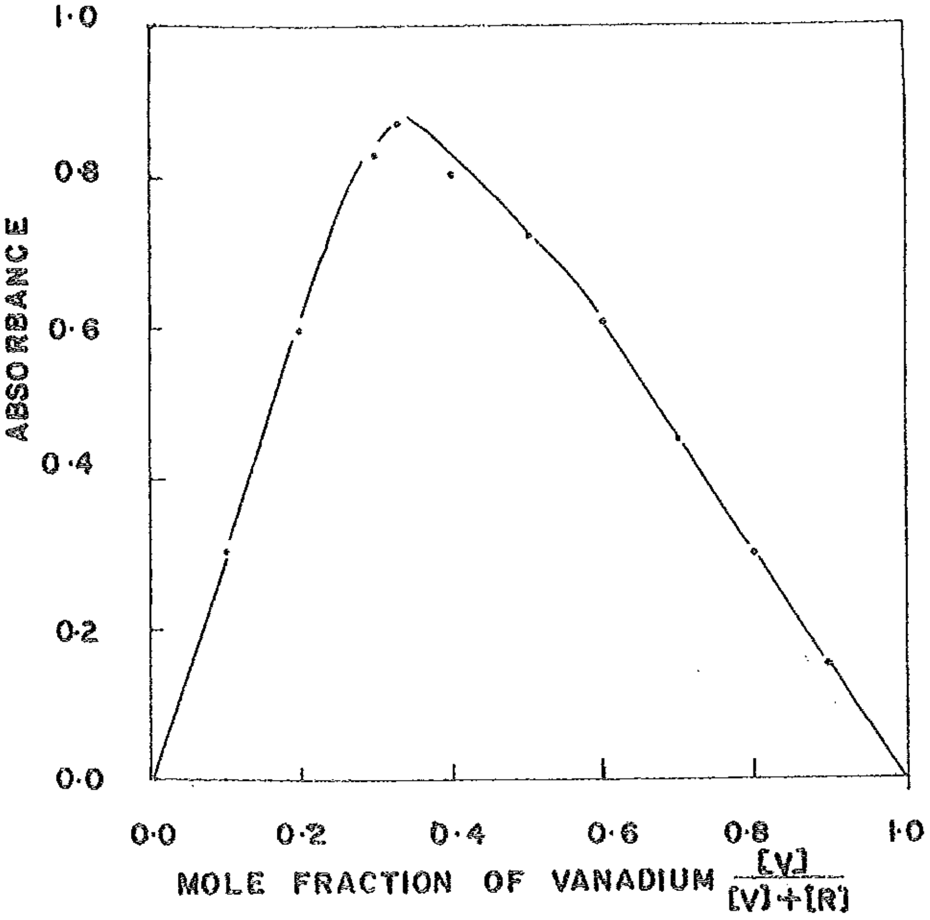


Fig. 14 JOB'S METHOD OF CONTINUOUS VARIATIONS.

The absorbances were plotted against mole ratio of PCHA to vanadium (Fig. 15). The intersection of the two tangents corresponds to the mole ratio of 1:2 (vanadium: PCHA).

CURVE FITTING METHOD: Both the concentrations of vanadium and PCHA were kept constant and only the concentration of thiocyanate was varied. Then absorbance were plotted against the molar concentration of thiocyanate in aqueous phase (Fig. 16). The slope of the curve indicates the combining ratio of 1:2 (vanadium to the thiocyanate). Hence the stoichiometric composition of the ternary complex is 1:2:2 (vanadium: PCHA: SCN).

The probable partition mechanism of the vanadium PCHA complex with and without the thiocyanate between water and chloroform is expressed as follows (45,53,55, 65,83,84).

Vanadium (V) reacts with PCHA to form 1:2(V: PCHA) complex extractable into chloroform

$$VO^{+}_{2aq} + 2HOA_{org} \rightleftharpoons VO(OA)_{2}OH_{org} + H^{+}_{aq}$$

and the equilibrium constant can be expressed as

$$\beta_{1,2} = \frac{[VO(OA)_{2}OH]_{org}\ [H^{+}]_{aq}}{[VO^{+}_{2}]_{aq}\ [HOA]^{2}_{org}}$$

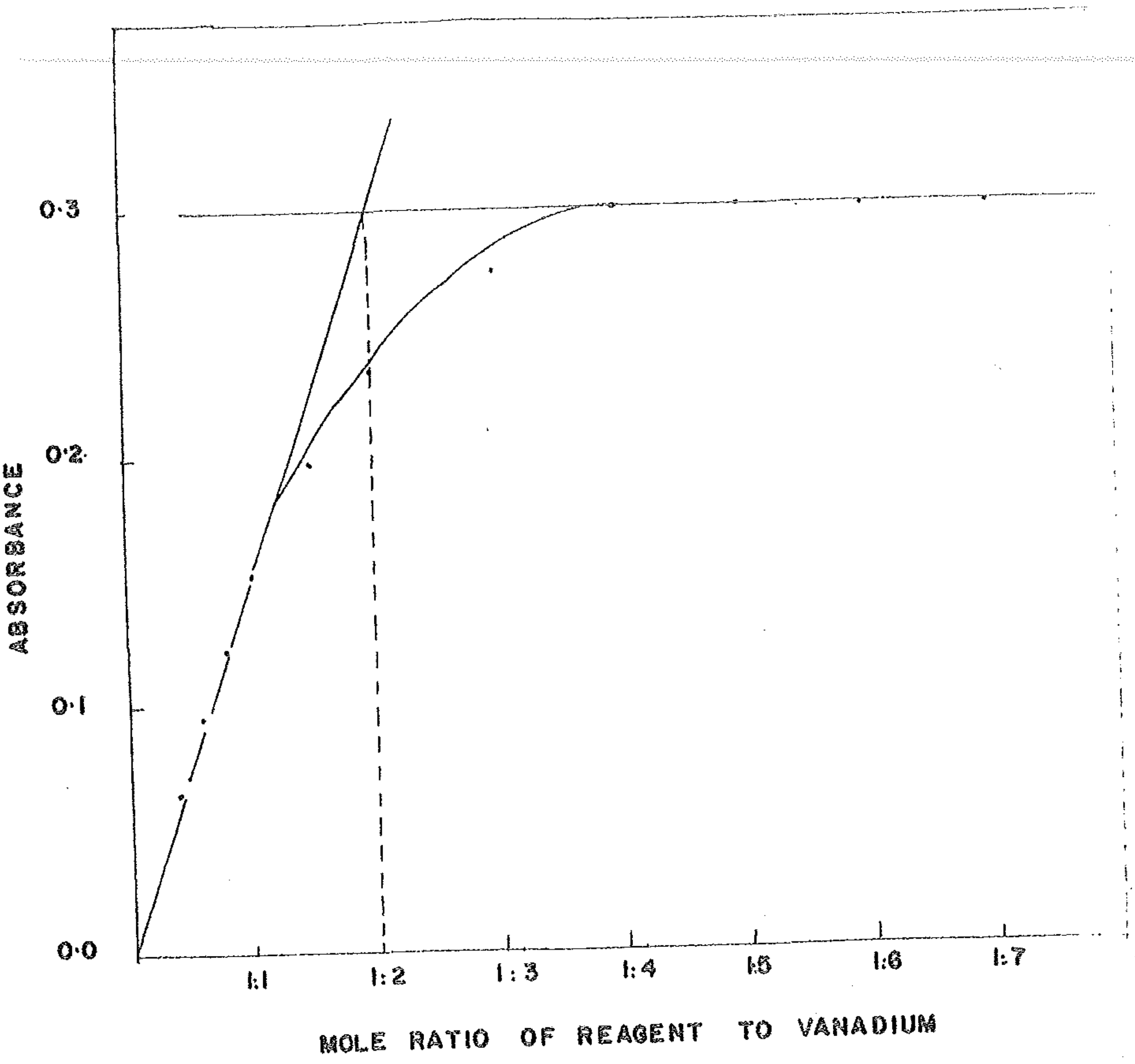


Fig. 16 MOLE RATIO METHOD

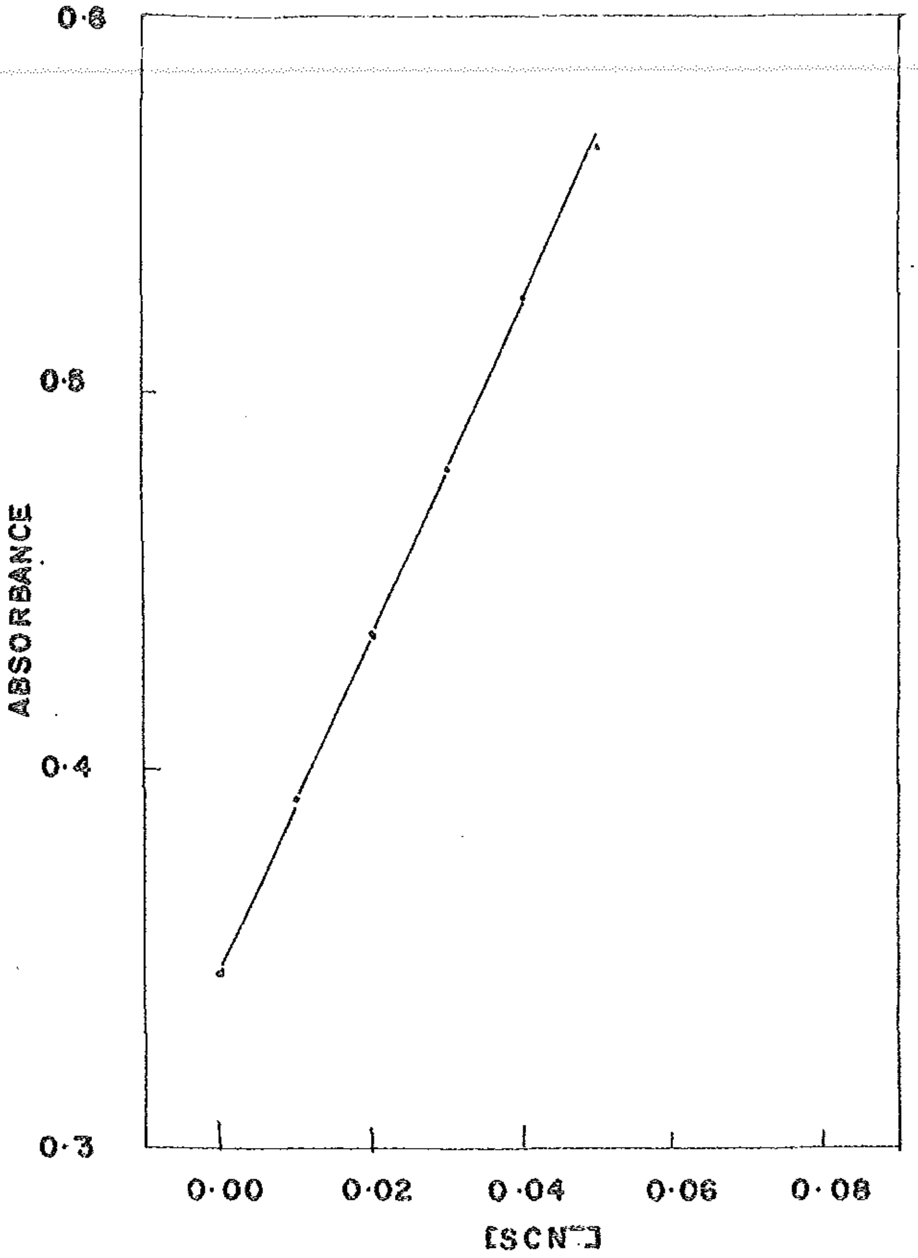


Fig.16 CURVE FITTING METHOD

The vanadium-PCHA complex reacts with thiocyanate to give 1:2:2 (V: PCHA: SCN) ternary complex

$$VO(OA)_2OH_{org} + 2SCN^-_{aq} + H^+_{aq} \rightleftharpoons VO(OA)(SCN)_2 \cdot HOA_{org} + OH^-_{aq}$$

which is defined by the equilibrium constant

$$\beta_{1,2,2} = \frac{[VO(OA)(SCN)_2 \cdot HOA]_{org}\ [OH^-]_{aq}}{[VO(OA)_2OH]_{org} \cdot [SCN^-]^2_{aq}\ [H^+]_{aq}}$$

Thus the overall extraction mechanism may be expressed as

$$VO^+_{2\,aq} + 2SCN^-_{aq} + 2HOA_{org} \rightleftharpoons VO(SCN)_2OA \cdot HOA_{org} + OH^-_{aq}$$

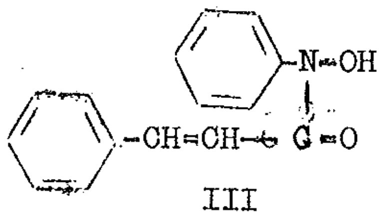
and the extraction constant is given by

$$Kex = \frac{[VO(SCN)_2OA \cdot HOA]_{org}\ [OH^-]_{aq}}{[VO^+_{2\,aq}\ [SCN^-]^2_{aq}\ [HOA]^2_{org}}$$

The distribution ratio is given by

$$D_{1,2,2} = \frac{[VO(SCN)_2OA \cdot HOA]_{org} + [VO(OA)_2OH]_{org}}{[VO^+_2]_{aq}}$$

$$= \beta_{1,2}[HOA]^2_{org}\ ([H^+]^{-1}_{aq} + \beta_{1,2,2}[SCN^-]^2_{aq}[OH^-]^{-1})$$


III

PCHA is a highly sensitive and selective spectrophotometric reagent for metals because of the presence of double bond in conjugation with carbonyl group in the molecule and hence it also finds extensive applications in spot test for metal ions. Hence, N-phenylcinnamohydroxamic acid has been employed for exploring its analytical potentialities.

A number of monobasic and bidentate chelating agents recommended for the spectrophotometric determination of vanadium react with the metal to form 1:2 (metal: ligand) coloured complexes extractable into various organic solvents (39 - 49). These vanadium complexes contain a basic V = O group and an acidic V - OH group in the same molecule (49 - 53).

The basic V = O group of the vanadium complex reacts with acidic substances like carboxylic acids and phenols to give a hyper and bathochromic shift (52 - 55) and the acidic V - OH group reacts with

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and mixed ligand complex accompanied by hyper and bathochromic shift. These colour reactions are capable of forming the basis for the development of sensitive and selective methods for the extraction and photometric determination of vanadium (V).

III. EXPERIMENTAL

3.1 SYNTHESIS OF N-ARYLHYDROXAMIC ACIDS

Yale (15) has described the various methods of the synthesis of hydroxamic acids. Out of the methods described for the synthesis of N-arylhydroxamic acids, the most commonly followed method is a suitable application of a method called Method B, which is an application of Schoten Baumann's reaction which involves the acylation of N-arylhydroxylamine with acid chloride in weakly basic medium. To improve the yield and purity of the reaction product several modifications have been made. In general, the N-arylhydroxamic acids are prepared by the modified method of Priyadarshini and Tandon (33). According to this modification N-arylhydroxamic acids are prepared by the condensation of N-arylhydroxylamines with acid chlorides at low temperature in diethylether medium made alkaline with aqueous suspension of sodium bicarbonate. The N-arylhydroxamic acids are purified by recrystallization from a mixture of benzene and petroleum ether. The yield range from 50 - 90/.

In the present study N-phenylcinnamohydroxamic

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acid was prepared by the modified method of Priyadarshini and Tandan (33). This required the preparation of cinnamoyl chloride and N-Phenylhydroxylamine.

PREPARATION OF CINNAMOYLCHLORIDE

Cinnamoyl chloride used for the synthesis of hydroxamic acid was prepared by the action of excess of thinoylchloride on cinnamic acid (37).

Cinnamic acid and thionylchloride were mixed in 1:1.5 molar ratio and refluxed over the boiling water bath for 2 hours. A clear solution of cinnamoylchloride was obtained. The unreacted thionyl chloride and cinnamoyl chloride were separated by fractional distillation under reduced pressure. The yield of acid chloride was 90/.

PREPARATION OF N-PHENYLHYDROXYLAMINE

N-Phenylhydroxylamine was prepared by the reduction of nitrobenzene with zinc dust and ammonium chloride in aqueous solution at 60 - 65°C (38).

The nitrobenzene was mixed with hot water and zinc dust was added gradually during the course of 30 minutes with stirring. The temperature was kept at 60 - 65°C throughout the reaction. After the addition of zinc dust, white zinc oxide was filtered off and the filtrate was saturated with salt. The hydroxylamine obtained on cooling the solution was filtered off and recrystalized from a mixture of benzene and petroleum ether.

The hydroxylamine used for the synthesis of hydroxamic acid was freshly prepared.

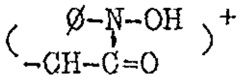
PROCEDURE FOR THE SEYNTHESIS OF N-PHENYLCINNAMO HYDROXAMIC ACID (PCHA)

A freshly crystallized N-phenylhydroxylamine (0.10 mole) was dissolved in 100 ml of diethylether and taken in a 500 ml conical flask. A fine suspension of 0.15 mole sodium bicarbonate in 20 ml of water was added to it. The flask was kept in a freezing mixture and the contents were stirred, to this, a solution of 0.10 mole of cinnamoylchloride in 100 ml of diethyelether was added dropwise during the course of one hour. Stirring was continued for additional 15 minutes and the temperature was maintained throughout at 0^{o}. A yellowish white precipitate of hydroxamic acid was obtained. The ethereal mother liquor was separated and ether removed. The combined solids were triturated with an ice cold saturated solution of sodium bicarbonate in a mortar for about 15 minutes to remove acidic impurities. The solid hydroxamic acid was filtered off under suction, washed with cold water and dried in air. The hydroxamic acid was purified by crystallization from a mixture of benzene and petroleum ether (boiling range 60 - 80°C). The yield was 70/. Mp 162°C [lit. 163°C (33)] MS: M^+ 239. The mass spectrum is given in Figure 1.

In the spectrum peaks are observed at M/es of 239 (mol. ion), 223, 168, 149, 131 (base peak), 103, 77, etc. Possible ion fragments corresponding to each are given in Table 1

Table 1

ION FRAGMENTS OF N-PHENYLCINNANOHYDROXAMIC ACID

M/e	Fragments
239	molecular ion
223	loss of an oxygen atom
168	$(\text{Ø-NH-Ø})^+$
149	 $\left(\begin{array}{l}\quad\text{Ø-N-OH}\\ \text{-CH-C=O}\end{array}\right)^+$
131	$(\text{Ø-CH=CH-C=O})^+$
103	$(\text{Ø-CH=CH})^+$
77	$(\text{Ø})^+$

solution was stable for several days when stored in amber bottles.

Colour Reaction: PCHA reacts with vanadate ions to form a bluish-violet complex in strong hydrochloric acid medium. The complex extracted into chloroform reacts with phenols giving rise to a hyper and bathochromic effect. The colour of chloroform extracts are different with different phenols.

General Procedure: To a separatory funnel, transfer an aliquot of the sample solution containing 15 - 150 µg of vanadium and add distilled water and then add strong hydrochloric acid until the volume is about 25 ml and the acidity between 1 and 3M. Add 5 ml of 0.2/ reagent solution and 10 ml of 1M phenol solution in chloroform. Shake the mixture vigorously for about 2 minutes. Allow the phases to separate for two minutes. Collect the organic phase in a 50 ml beaker containing about 2g of anhydrous sodium sulphate. Wash the aqueous phase twice with 2 to 3 ml portions of chloroform to remove any residual colour and add the washings to the contents of the beaker. Decant the coloured solution from the beaker into a 25 ml volumetric flask. Wash out the adhering colour from sodium sulphate crystals with small portion and chloroform. Mix the washings with main solution and dilute to the mark with chloroform.

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Measure the absorbance at the wavelength of maximum absorption against reagent blank. Whenever the reagent blank was colourless, it was replaced by chloroform.

COMPOSITION OF THE COMPLEX

Composition of the vanadium -PCHA-p-chlorophenol complex was studied following the methods below.

METHOD OF CONTINUOUS VARIATIONS

PROCEDURE: X ml of 1.0×10^{-3}M solution of vanadium, (10-x) ml of water and 5 ml of 6M hydrocloric acid were transfered into a separatory funnel. (10-x) ml of 1.0×10^{-3}M solution of PCHA, xml of chloroform and 5 ml of 2M p-chlorophenol in chloroform were added to it, thus the volumes of the aqueous and organic phases were 15 ml. The contents of the funnel were shaken vigorously for two minutes and the phaseswere allowed to separate. Then proceeded as described earlier. The absorbances of the solutions were measured at 565 nm and plotted against the mole fraction of the vanadium.

MOLE RATIO METHOD

PROCEDURE: 1 ml of 1.963×10^{-3}M solution of vanadium 9 ml of water and 5 ml of 6M HCl were taken in a separatory funnel. Xml of 1.963×10^{-3} solution of PCHA, (10-x)ml of chloroform and 5 ml of 2M phenol were added

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to it, thus the volume of the aqueous and organic phases were equal to 15 ml. The contents of the funnel were shaken vigorously for two minutes then proceeded as described earlier.

CURVE FITTING METHOD

PROCEDURE: 1.5 ml of 1.77 X 10^{-3}M solution of vanadium 8.5 ml of water and 5 ml of 6M $CHCl_3$ were taken in a separatory funnel. 5 ml of 0.2/ solution of PCHA, Xml of 1M p-chlorophenol and (10-x)ml of chloroform were added to it, thus volumes of the aqueous and the organic phases were equal to 15 ml. The contents of the funnel were shaken vigorously for two minutes and then proceeded as described earlier.

APPLICATION OF THE METHOD

PROCEDURE: A weighed amounts of sample containing approximately 1 mg of vanadium was transferred in a 400 ml beaker and dissolved with nitric acid. Tungsten was precipitated as tungstic acid. It was filtered off and washed thoroughly. The filterate was evaporated to nearly dryness, dissolved in water and finally transferred to a 100 ml volumetric flask and diluted to the mark. A 10 ml aliquote of the solution was pipetted into a 100 ml separatory funnel, and vanadium was determined according to the general procedure.

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for 2 minutes and the phases were allowed to separate. Then proceeded as in the recommended procedure.

MOLE RATIO METHOD

PROCEDURE: 1 ml of 1.0 X 10^{-3}M solution of vanadium, 9 ml of water and 5 ml 15M acetic acid were taken in a separatory funnel. Xml of 1.0 x 10^{-3}M solution of PCHA and (15 - X)ml chloroform were added to it and the content contents of the funnel were shaken vigorously for one minute. Then 5 ml 1M thiocyanate solution was added to the funnel and the contents were again shaken vigorously for two minutes and proceeded as in the recommended procedure.

CURVE FITTING METHOD

PROCEDURE: 1 ml of 2.0 X 10^{-3}M solution of vanadium, and 4 ml of 10M acetic acid were transfered to a separatory funnel. 10 ml of 2.0 X 10^{-3}M solution of PCHA was added to it and the contents of the funnel were shaken vigorously for one minute. Then X ml of 0.5M thiocyanate and (5 - X)ml of water were added to funnel and the contents were again shaken vigorously for 2 minutes and then proceeded as in the recommended procedure.

IV. RESULTS AND DISCUSSION

4.1 VANADIUM (V)-PCHA+p-CHLOROPHENOL COMPLEX

4.1.1 Absorption Spectra: The absorption spectra of the reagent and the vanadium (V)-PCHA complex in the absence and presence of phenols are shown in Figure 2 and 3. The reagent showed negligible absorption in the region 450 - 700 nm. The bluish-violet vanadium PCHA complex in the absence of phenols showed a broad maximum absorption around 540 nm with molar absorption coefficient of 6200 $l \cdot mole^{-1} cm^{-1}$. In the presence of phenols a strong hyperchromic and bathochromic effect of the adduct in chloroform solution is observed. As shown in figure 3 when phenols are added to the chloroform solution of vanadium (V)-PCHA complex the wavelengths of maximum absorption shifts to longer wavelengths and absorbance increases with increasing concentration of phenols. At higher concentration of phenols more than 0.3M both the wavelengths of maximum absorption and absorbances remain constant.

The wavelengths of maximum absorption and molar absorbtivities of the resulting complexes are different for different phenols as shown in Table 2.

Of the various phenols used, the adduct formed with p-chlorophenol has highest value for the molar absorptivity. Hence, detailed studies were carried out with p-chlorophenol.

TABLE 2

SPECTRAL CHARACTERISTICS OF VANADIUM (V) -PCHA-PHOH COMPLEXES IN CHLOROFORM

Phenol	[Phenol] M	λ-max nm	ϵ l-mole^{-1}cm^{-1}	Sensitivity μgVcm^{-2}
None	–	540	6200	0.0082
o-Dichlorophenol	0.2	555	6300	0.0080
Benzonaphthol	0.2	550	6200	0.0082
Benzylphenol	0.3	560	7350	0.0069
p-Chlorophenol	0.3	565	7500	0.0068

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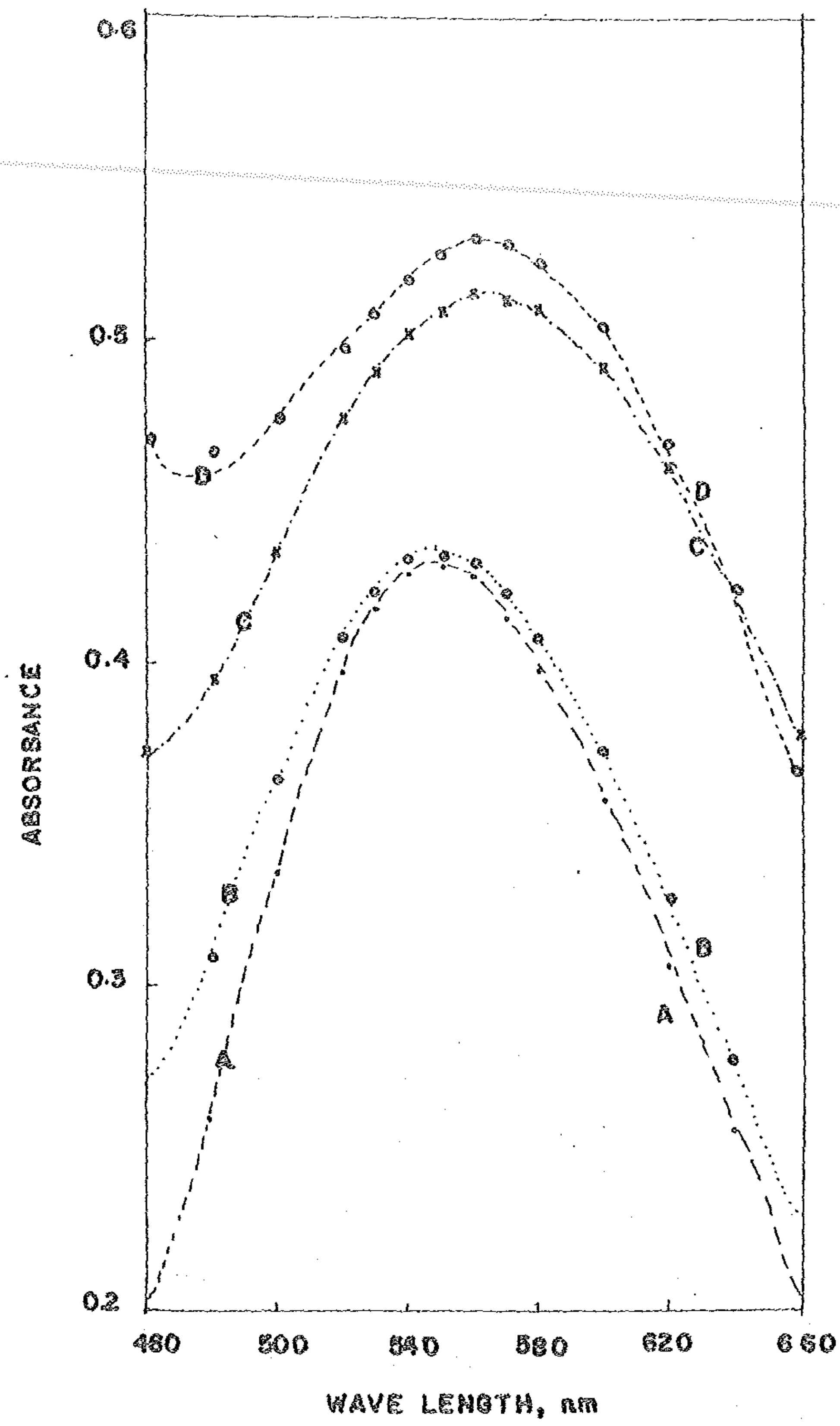

Fig.2 ABSORBTION SPECTRA OF VANADIUM(V)- PCHA COMPLEX IN THE PRESENCE OF PHENOLS
A. BENZONAPHTHOL B:1,2- DICHLOROPHENOL
C. BENZYLPHENOL D: P- CHLOROPHENOL
($C_V = 7.07 \times 10^{-6}$ M, $C_{PhoH} = 2.4 \times 10^{-1}$ M)

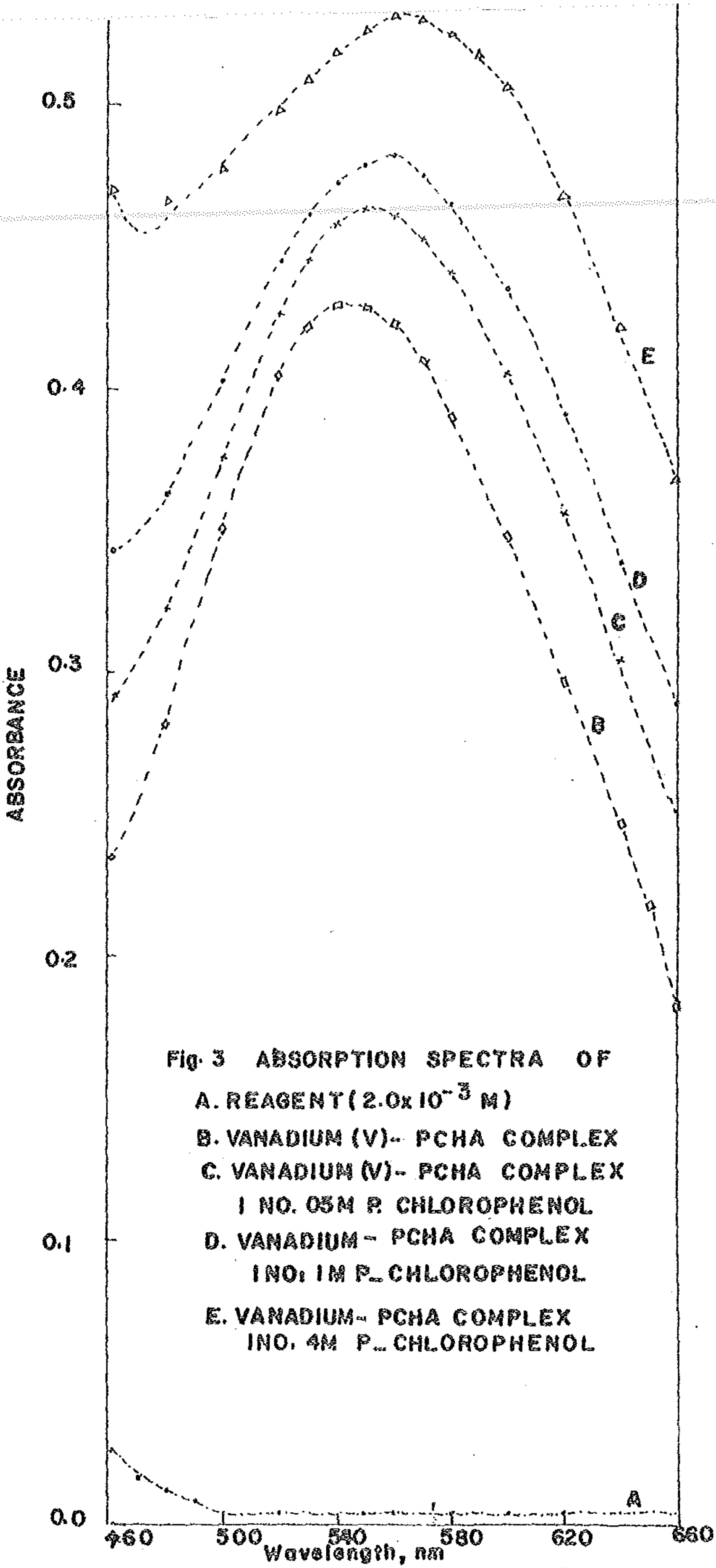

Fig. 3 ABSORPTION SPECTRA OF
A. REAGENT (2.0×10^{-3} M)
B. VANADIUM (V)- PCHA COMPLEX
C. VANADIUM (V)- PCHA COMPLEX
I NO. 05M P. CHLOROPHENOL
D. VANADIUM - PCHA COMPLEX
INO. I M P- CHLOROPHENOL
E. VANADIUM- PCHA COMPLEX
INO. 4M P- CHLOROPHENOL

4.1.2 EFFECT OF VARIABLES: The effect of several experimental variables on the extraction of vanadium (V)-PCHA complex in presence of p-chlorophenol has been investigated. The effect of particular variable was studied by determining vanadium following the general procedure described earlier, keeping all the experimental parameters constant except the one under the study.

CHOICE OF SOLVENT FOR EXTRACTION: The vanadium complex can be extracted by several organic solvents such as chloroform, carbontetrachloride, 1,2-dichlorobenzene, benzene, toluene, o-xylene and diethylether. Chloroform was found to be the most suitable solvent for extraction of the vanadium complex. It was also preferred because of its low cost, easy to recover, relatively higher solubility of PCHA in it than in other solvents and its high extracting effect toward the adduct.

Acidity: The extraction and determination of vanadium was studied in the absence and presence of p-chlorophenol and are given in Table 3 and 4 and Figure 4. In the absence of p-chlorophenol the optimum acidity range, for the complete extraction of vanadium, was found to be 3.0÷7.5M. whereas in the presence of p-chlorophenol it was found to be 1 - 3M with respect to hydrochloric acid. It should be noted that extraction of vanadium in the presence of p-chlorophenol occurs at a lower acidity than that in the absence of phenol, i.e. synergic extraction of vanadium is observed in the presence of p-chlorophenol. The synergic extraction can be explained by the formation of the adduct which is described later in this chapter.

TABLE 3

EFFECT OF HYDROCHLORIC ACID CONCENTRATION OF THE AQUEOUS PHASE ON THE EXTRACTION OF VANADIUM-PCHA COMPLEX INTO CHLOROFORM.

Vanadium concentration = 90µg/25 ml

Concentration of hydrochloric acid in aqueous phase M	Absorbance at 565 nm
0.0	0.118
1.0	0.272
2.0	0.381
2.5	0.412
3.0	0.430
4.0	0.432
5.0	0.430
6.0	0.431
7.0	0.429
7.5	0.430
8.0	0.413
9.0	0.365

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TABLE 4

EFFECT OF HYDROCHLORIC ACID CONCENTRATION OF THE AQUEOUS PHASE ON THE EXTRACTION OF VANADIUM-PCHA-p-CHLOROPHENOL COMPLEX INTO CHLOROFORM

Vanadium concentration = 90µg/25 ml

Concentration of hydrochloric acid in aqueous phase M	Absorbance at 565 nm
0.0	0.433
1.0	0.529
2.0	0.531
3.0	0.530
4.0	0.483
5.0	0.430

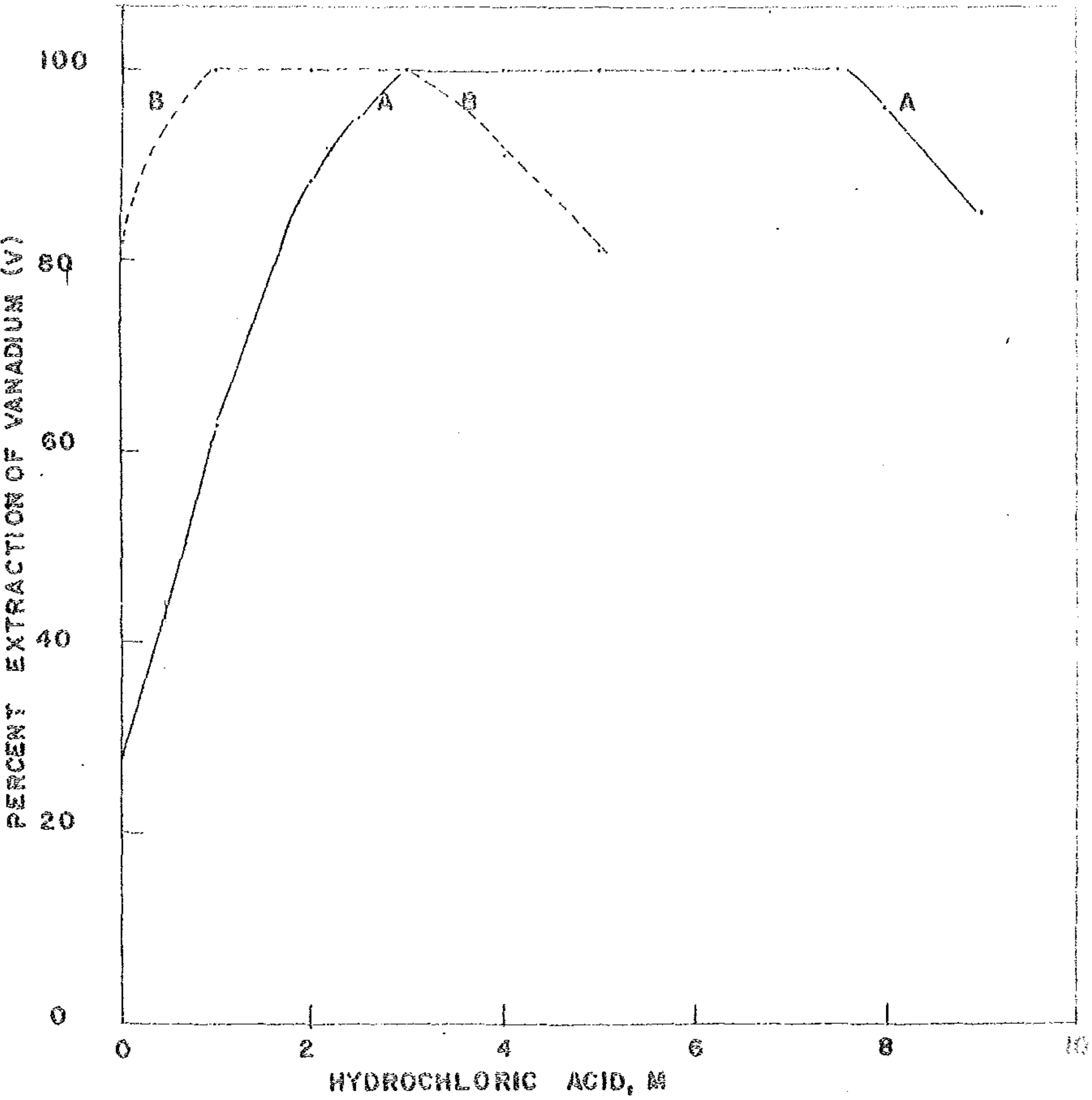

Fig.4 EFFECT OF ACIDITY OF AQUEOUS PHASE ON EXTRACTIO
OF VANADIUM (V)- PCHA COMPLEX

A· IN THE ABSCENCE OF P-CHLOROPHENOL
B· IN THE PRESENCE OF P-CHLOROPHENOL

Workers (76, 77) reported the reduction of vanadium (V) to vanadium (IV) in concentrated hydrochloric acid solution, however, the reduction is negligible in lower concentration (78). Thus in the presence of phenol, there is no danger of the reduction of vanadium (V) in the lower acidity range.

AMOUNTOF PCHA: A 1:6 molar ratio of the reagent to vanadium was adequate for complete extraction of vanadium. A large excess of the reagent upto 50 fold molar excess has no influence on the extraction and determination of vanadium. In practice, a 20 fold molar excess of the reagent was employed for the extraction of vanadium. The results are shown in Table 5.

AMOUNT OF P-CHLOROPHENOL: As shown in Table 6, the absorbance increases with increasing amount of phenol from 1:94 to 1:943 and remains constant from 1:943 to 1:1887 molar ratios of vanadium to phenol. Absorbance again increases with further increase in phenol from 1:1887 to 1:2830 and finally becomes constant at higher concentration of phenol. These results indicate the formation of two complexes depending on the concentration of phenol.

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TABLE 5

EFFECT OF AMOUNT OF REAGENT, PCHA

Vanadium concentration = 100µg/25 ml
concentration of hydrochloric acid
in aqueous phase = 2.0M

Mole ratio of reagent to vanadium	Absorbance at 565 nm
0.5:1	0.142
1.0:1	0.285
1.5:1	0.380
2.0:1	0.448
2.5:1	0.500
3.0:1	0.530
3.5:1	0.549
4.0:1	0.562
5.0:1	0.580
6.0:1	0.588
8.0:1	0.590
10.0:1	0.589
20.0:1	0.590
50.0:1	0.592

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TABLE 6

EFFECT OF p-CHLOROPHENOL

Vanadium concentration = 135µg/25 ml
(1.06×10^{-4}M)

Hydrochloric acid concentration of
the aqueous phase = 2M

Mole ratio of vanadium to p-chlorophenol	Molar concentration of p-chlorophenol	Absorbance at 565 nm
1:94	0.01	0.640
1:189	0.02	0.649
1:283	0.03	0.660
1:377	0.04	0.671
1:472	0.05	0.682
1:566	0.06	0.691
1:660	0.07	0.700
1:755	0.08	0.706
1:943	0.10	0.709
1:1415	0.15	0.710
1:1981	0.21	0.723
1:2075	0.22	0.737
1:2170	0.23	0.750
1:2264	0.24	0.764
1:2358	0.25	0.776
1:2830	0.30	0.795
1:3773	0.40	0.795
1:4717	0.50	0.794
1:5660	0.60	0.796

ORDER OF ADDITION OF REAGENT: It was found that there is no change in the absorbance or in colour intensity of the complex if the order of addition of reagents is changed.

TIME: The complex is completely extracted into chloroform within two minutes. Chloroform extracts of the complex are stable for several days and hence the time of measurement of absorbance is not critical. The absorbance of the solution measured after seven days remains constant (Table 10).

VOLUME RATIO: The volume of the aqueous and organic phase can vary from 1:1 to 1:5 without any adverse effect on absorbance value or extraction efficiency (Table 7).

IONIC STRENGTH AND TEMPERATURE: No significant effect was noted on the absorbance of the coloured systems or the percent extraction of vanadium when the ionic strength of the aqueous phase was adjusted between 1 and 4M with hydrochloric acid and potassium chloride. Variation in temperature of the aqueous phase from 20 to 36°C did not produce any measurable change in the absorbance of the chloroform extracts (Table 8 and 9).

4.1.3 BEER'S LAW; OPTIMUM CONCENTRATION RANGE, SENSITIVITY AND MOLAR ABSORPTIVITY: The coloured system obeys Beer's low from 0.6 to 7.2 ppm of vanadium at 565 nm.

TABLE 7

EFFECT OF VOLUME OF AQUEOUS PHASE

Vanadium concentration = 100µg/25 ml

Volume of the organic phase = 15 ml

Volume of the aqueous phase ml	Absorbance at 565 nm
05	0.586
10	0.591
20	0.590
30	0.592
40	0.588
50	0.590

TABLE 8

EFFECT OF IONIC STRENGTH OF THE AQUEOUS PHASE

Vanadium concentration = 100µg/25 ml

Hydrochloric acid concentration of the aqueous phase = 1.0M

Concentration of KCl in the aqueous phase M	Absorbance at 565 nm
0	0.591
1	0.590
2	0.587
3	0.592
4	0.589

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TABLE 9

EFFECT OF TEMPERATURE OF THE AQUEOUS PHASE

Vanadium concentration = 100ug/25 ml

Hydrochloric acid concentration = 2.0M

Temperature of the aqueous phase °C	Absorbance at 565 nm
20	0.591
25	0.590
30	0.592
35	0.590

TABLE 10

STABILITY OF THE EXTRACT

Vanadium concentration = 100 µg/25 ml
Hydrochloric acid concentration of
the aqueous phase = 2.0M

Time of measurement after extraction hour	Absorbance at 565 nm
0	0.587
3	0.593
6	0.590
12	0.592
24	0.587
48	0.589
72	0.590
96	0.586
120	0.588
144	0.590
168	0.591

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(Table 11, Figure 5) and the optimum concentration range for the determination as evaluated from the Ringbom's plot (60) is 1.5 to 5 ppm of vanadium (Fig. 6). The photometric sensitivity (61) of the colour reaction and the molar absorbtivity are 0.0068 μg of vanadium per square cm and 7500 ± 70 liter $mole^{-1}cm^{-1}$ at 565 nm respectively.

4.1.4 PRECISION: Ten independent determinations on solutions each containing a final vanadium concentration 2.72 ppm gave a mean absorbance of 0.400 with a standard deviation of ± 0.002. The value of relative standard deviation is ± 0.5/. These observations suggest that the method is fairly precise and gives reproducible results.

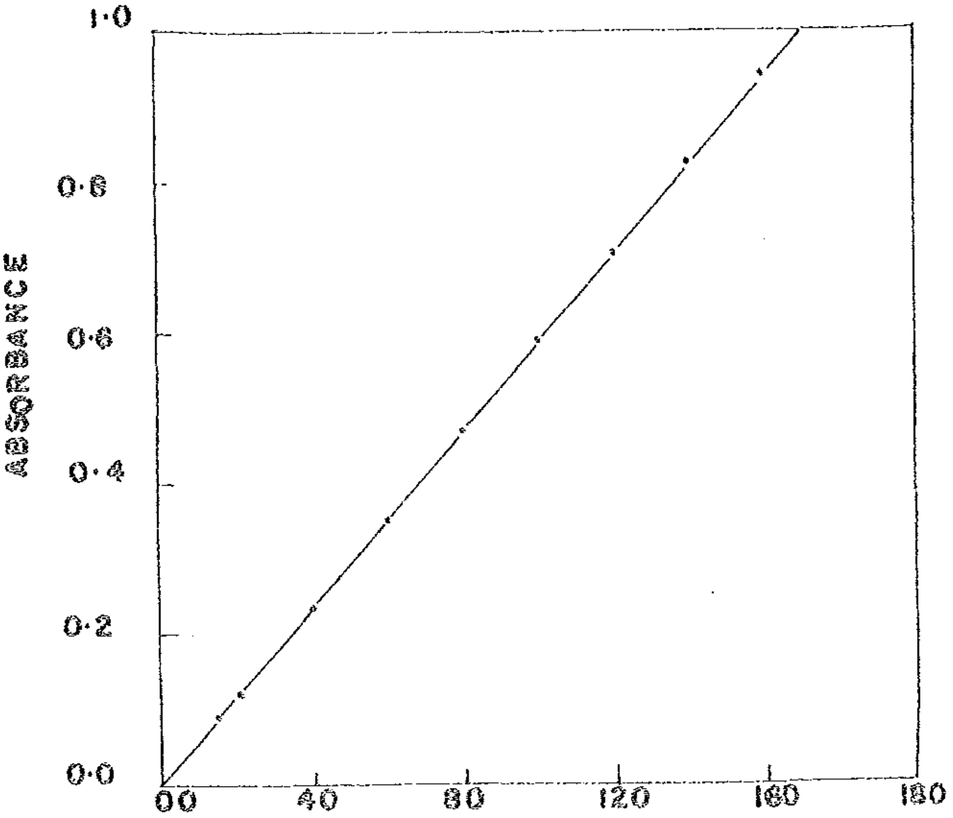
4.1.5 INFLUENCES OF DIVERSE IONS: For studying the effect of diverse ions on the coloured system, an aliquot of standard vanadium solution containing 90 μg of vanadium (V) was transferred to separatory funnel and to this was added a solution containing a known quantity of the desired diverse ion. The acidity of the solution was adjusted between 2M and 3M hydrochloric acid. Vanadium was extracted and determined

TABLE 11

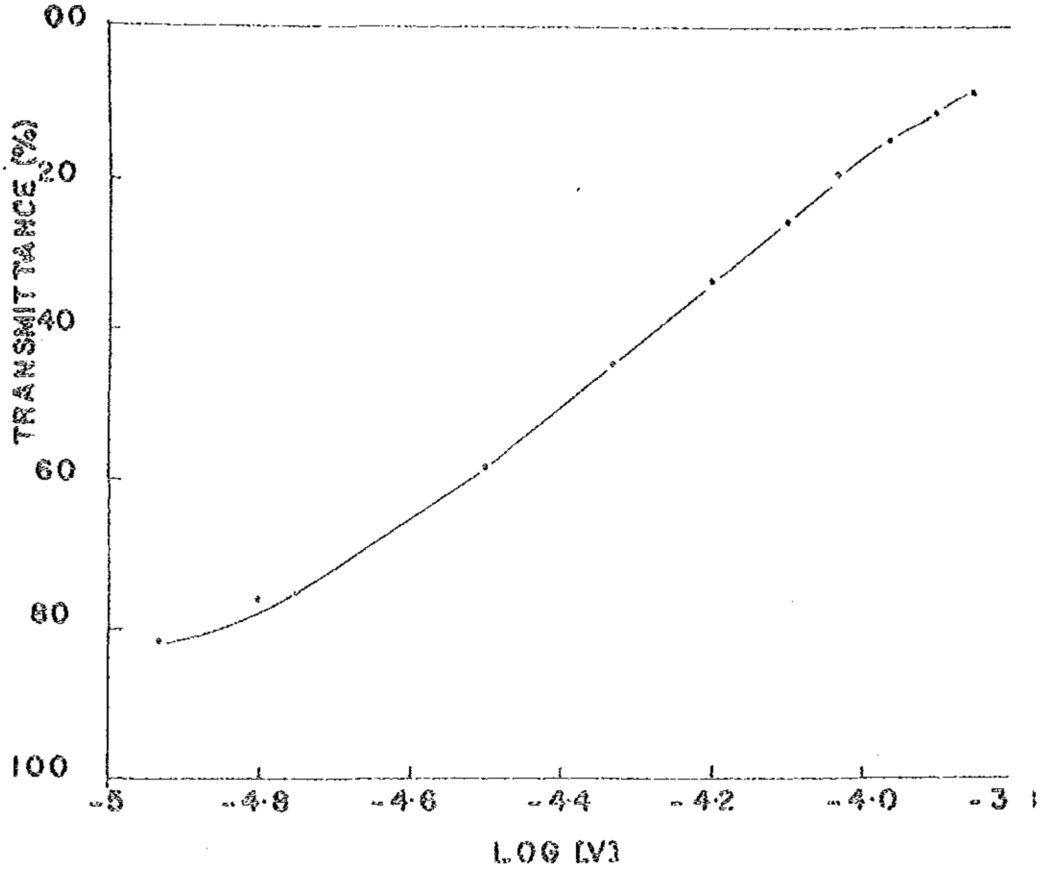
CALIBRATION CURVE DATA FOR THE DETERMINATION OF VANADIUM (V)

Concentration of hydrochloric acid in aqueous phase = 2M.

Vanadium (V)µg/25 ml in chloroform	Absorbance at 565 nm
15	0.088
20	0.118
40	0.235
60	0.353
80	0.471
100	0.589
120	0.707
140	0.824
160	0.942
180	1.060



Fig·5 CALIBRATION CURVE FOR DETERMINATION OF VANADIUM(V)



Fig·6 RINGBOM'S PLOT TO DETERMINE THE EFFECTIVE CONCENTRATION OF VANADIUM (V) following the procedure described earlier. The tolerance limits for various diverse ions are given in Table 12.

Most of the common ions normally associated with vanadium do not interfere. Fe(III), Ti(IV), Zr(IV) and Mo(VI), which normally interfere in the determination of vanadium with other reagents do not interfere with PCHA in presence of p-chlorophenol. Tungsten (VI) inhibits colour development and extraction of vanadium when present in amounts greater than 5 ppm and thus should be removed prior to extraction and detemination of vanadium. The striking selectivity for vanadium (V) reaction with the reagent and especially the absence of interference of iron (III) is a feature of this method.

4.1.6 COMPOSITION OF THE COMPLEX

An attempt has been made to determine the stoichiometric composition of the complex formed between vanadium (V), PCHA and p-chlorophenol in chloroform. The ratio of vanadium to PCHA was determined by mole ratio (62), and continuous variation (63) methods. The ratio of vanadium to p-chlorophenol was evaluated by the curve fitting method (64).

TABLE 12

INFLUENCE OF FOREIGN IONS

Vanadium concentration = 90 µg/25 ml
= 3.6 ppm

Hydrochloric acid concentration of
the aqueous phase = 3M

Ion I	Added as II	Amount of ion added ppm, III	Absorbance at 565 nm, IV
None	–	–	0.530$^+$
Ag^+	$AgNO_3$	800	0.530
Al^{+3}	$Al(NO_3)_3$	800	0.525
As^{+5}	Na_3AsO_4	600	0.530
Ba^{+2}	$BaCl_2$	600	0.535
Be^{+2}	$BeSO_4$	800	0.530
Bi^{+3}	$Bi(NO_3)_3$	600	0.530
Ca^{+2}	$Ca(NO_3)_2$	1000	0.530
Cd^{+2}	$Cd(NO_3)_2$	800	0.525

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Table 12 (cont'd)

I	II	III	IV
Ce^{+4}	$(NH_4)_2Ce(NO_3)_6$	600	0.530
Co^{+2}	$Co(NO_3)_2$	800	0.530
Cr^{+3}	$Cr(NO_3)_3$	600	0.525
Cu^{+2}	$Cu(NO_3)_2$	1000	0.530
Fe^{+3}	$Fe(NO_3)_3$	1000	0.530
Ga^{+3}	$Ga(NO_3)_3$	600	0.535
Hg^{+2}	$Hg(NO_3)_2$	600	0.530
In^{+3}	$In(NO_3)_3$	600	0.525
La^{+3}	$La(NO_3)_3$	1000	0.530
Mg^{+2}	$Mg(NO_3)_2$	1000	0.530
Mn^{+2}	$Mn(NO_3)_2$	1000	0.530
Mo^{+6}	$(NH_4)_2MoO_4$	200	0.525
Ni^{+2}	$Ni(NO_3)_2$	1000	0.530
NH_4^+	NH_4NO_3	1000	0.530
Sn^{+4}	$SnCl_4$	400	0.535
Sr^{+2}	$Sr(NO_3)_2$	800	0.530
Th^{+4}	$Th(NO_3)_4$	1000	0.530

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Table 12 (cont'd)

I	II	III	IV
Ti^{+4}	$K_2TiO(C_2O_4)_2$	200	0.530
Tl^{+1}	Tl_2CO_3	800	0.525
U^{+6}	$UO_2(NO_3)_2$	800	0.530
W^{+6}	Na_2WO_4	10	0.525
Zn^{+2}	$Zn(NO_3)_2$	800	0.535
Zr^{+4}	$Zr(NO_3)_4$	200	0.530
Acetate	CH_3COONa	1000	0.530
Borate	$Na_2B_4O_7$	600	0.535
Citrate	$C_6H_8O_7$	800	0.530
Fluoride	NaF	600	0.530
Oxalate	$H_2C_2O_4$	800	0.530
Perchlorate	$HClO_4$	800	0.530
Phosphate	Na_2HPO_4	800	0.525
Tartrate	$C_4H_6O_6$	800	0.530

[+] Mean of 3 repeatitive analysis of the same sample.

The results obtained indicate the formation of two complexes depending upon the concentration of phenol. At lower concentration of phenol a 1:2:1 (Vanadium: PCHA: Phenol) complex is formed and at higher concentration of phenol a 1:2:2 (V: PCHA: PhOH) complex is formed.

METHOD OF CONTINUOUS VARIATIONS: An equimolar solutions of vanadium and PCHA were prepared. The mole fractions of vanadium and the reagent were varied with a constant total molarity in the presence of a constant excess of p-chlorophenol.

The maximum absorbance occured at a mole fraction of 0.33 ([V]/([V] + [PCHA])). This indicates the stoichiometric ratio of 1:2 (vanadium to reagent) in the complex (Table 13, Fig. 7).

MOLE RATIO METHOD: The concentration of vanadium was kept constant and the mole ratios of vanadium to PCHA were increased by increasing the concentration of PCHA in the presence of a constant excess of the phenol.

The absorbances were plotted against the mols ratio of PCHA to vanadium (Fig. 8). The two straight lines (the initial and final parts of the curve) were extrapolated which interesect each other at a mole ratio of 1:2 (vanadium to PCHA). This indicates the combining ratio of 1:2 (V: PCHA) in the complex.

CURVE FITTING METHOD: The concentrations of vanadium and PCHA were kept constant and the concentration of p-chlorophenol was varied.

To determine the ratio of vanadium (V) to phenol, the absorbance was plotted agains the molar concentration of p-chlorophenol.

As evident from Fig. 9 the curve has two inflection points. The slope of both straight parts of the curve approaches very closely to the integer 1. This

TABLE 13

JOB'S METHOD OF CONTINUOUS VARIATIONS

Concentration of vanadium solution = 1.0 X 10^{-3}M

Concentration of PCHA solution = 1.0 X 10^{-3}M

Concentration of p-chlorophenol in the organic phase = 0.4M

Hydrochloric acid concentration of the aqueous phase = 2M

Vanadium Xml	Water (10-x)ml	Reagent (10-x)ml	Chloroform Xml	Abssorbance at 565 nm
1	9	9	1	0.300
2	8	8	2	0.572
3	7	7	3	0.803
3.3	6.7	6.7	3.3	0.834
4	6	6	4	0.785
5	5	5	5	0.700
6	4	4	6	0.582
7	3	3	7	0.435
8	2	2	8	0.290
9	1	1	9	0.146

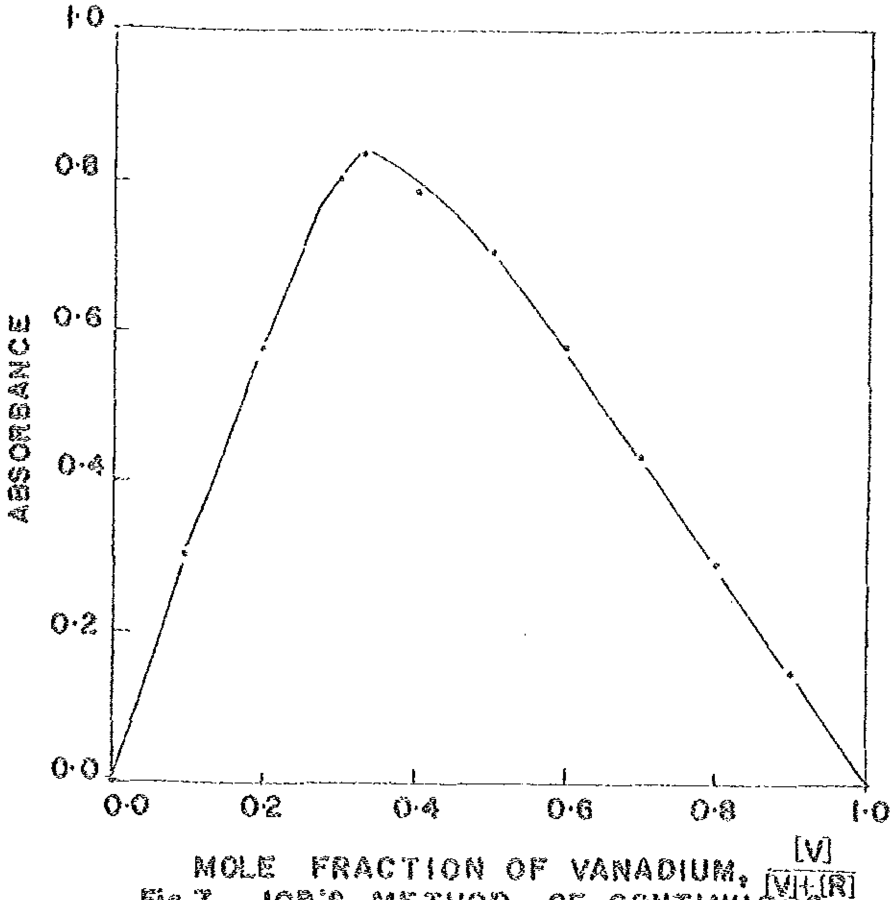

Fig.7 JOB'S METHOD OF CONTINUOUS VARIATIONS

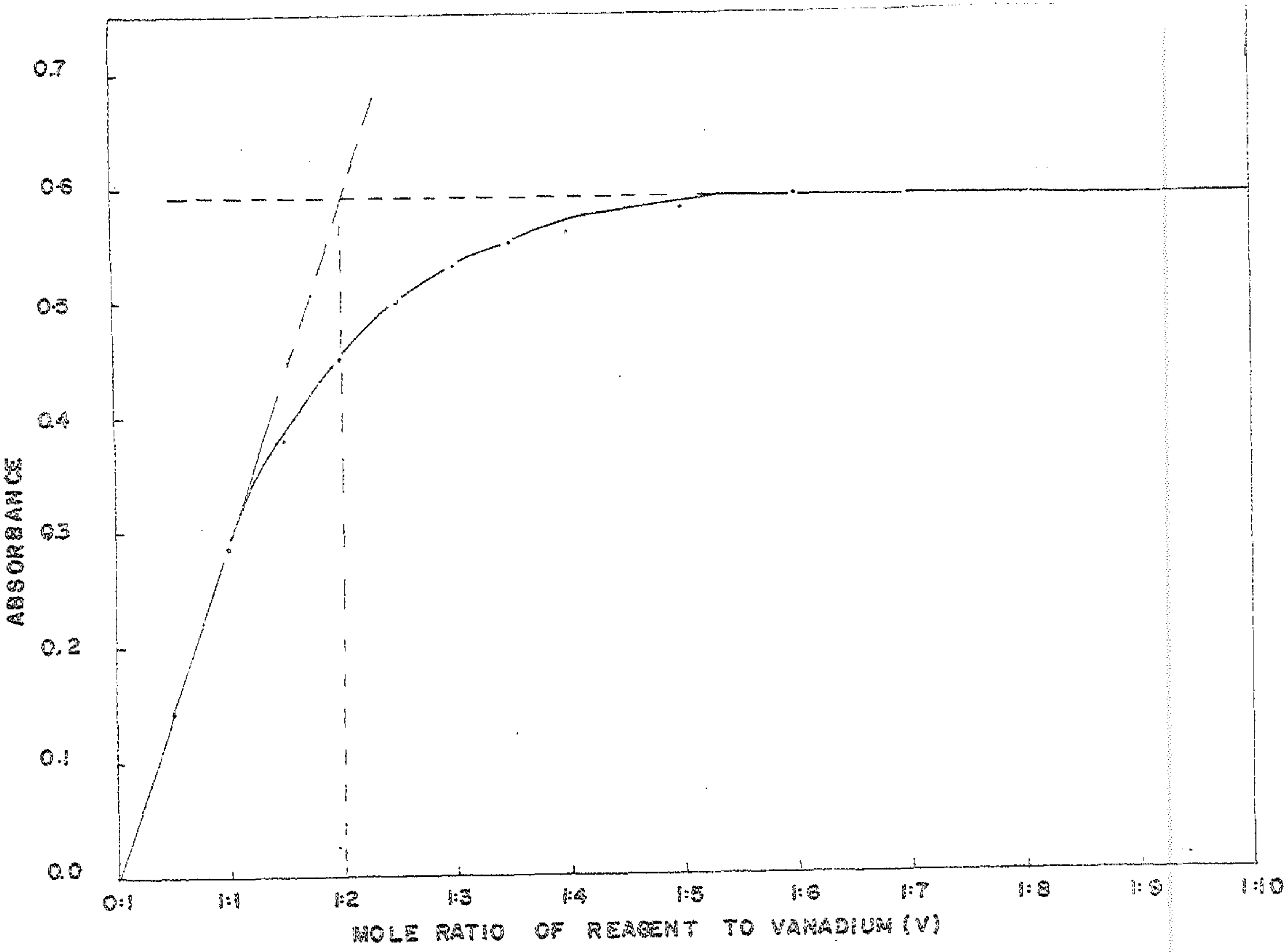

Fig.8 MOLE RATIO METHOD·

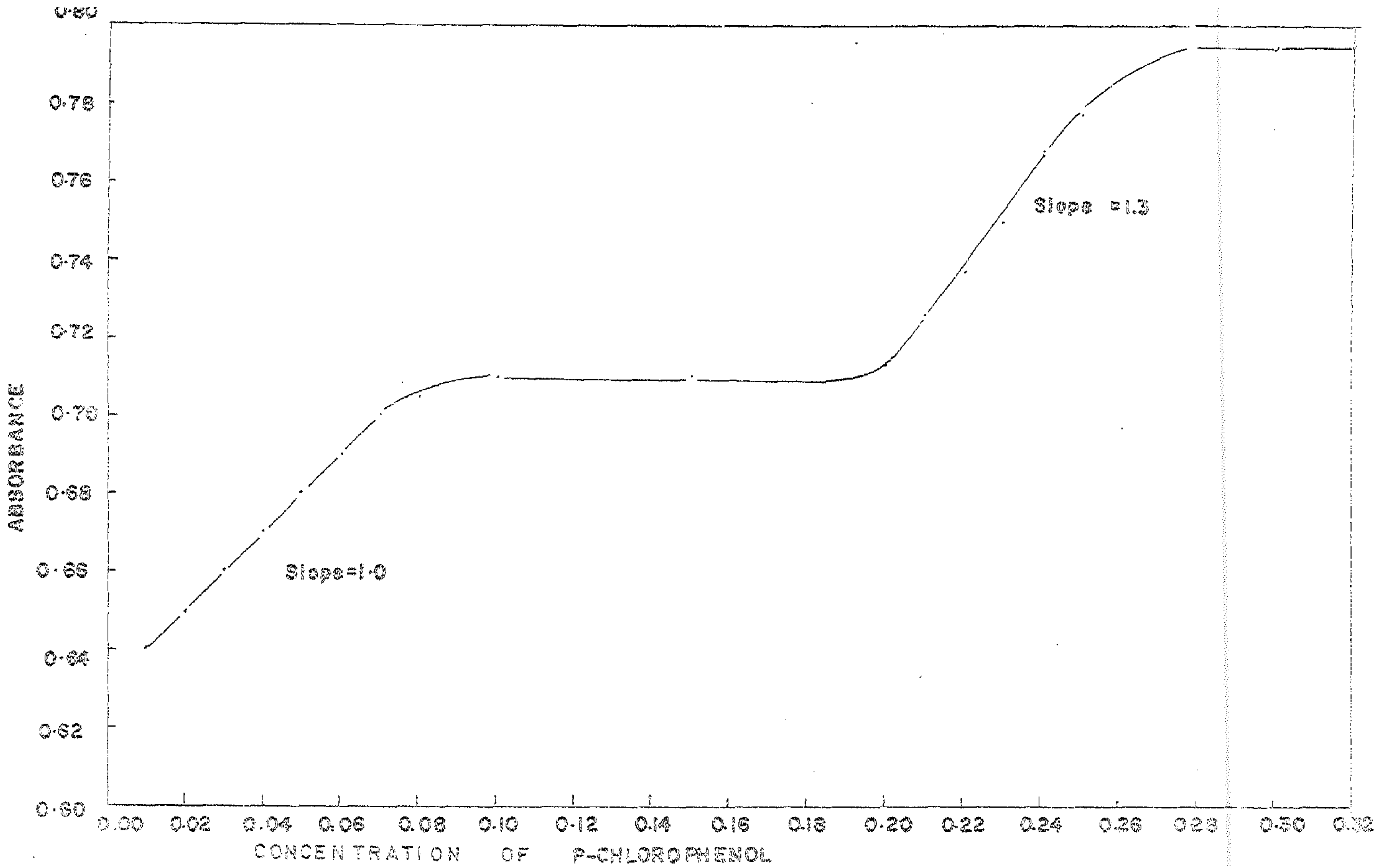

Fig. 9 CURVE FITTING METHOD

suggests the ratio of vanadium to p-chlorophenol to be 1:1 and 1:2 depending on the concentration of p-chlorophenol.

Thus, the results favour the formation of a 1:2:1 and 1:2:2 (metal/PCHA/p-chlorophenol) ternary complexes. The extraction equilibria may thus be expressed as follow (45,65,53,55):

In the absence of p-chlorophenol a 1:2 (metal: ligand) comples is extracted:

$$VO_{2\,aq}^{+} + 2HOA_{org} \rightleftharpoons VO(2OA)OH_{org} + H_{aq}^{+}$$

and the equilibrium constant is given by

$$\beta_{1,2} = \frac{[VO(2OA)OH]_{org}\ [H^+]_{aq}}{[VO_2^+]_{aq}\ [HOA]_{org}^2}$$

In the presence of p-chlorophenol, the reaction takes place in two steps. At lower concentration of p-chlorophenol a 1:2:1 adduct is formed

$$VO(2OA)OH_{org} + PhOH_{org} \rightleftharpoons VO(2OA)OH.PhOH_{org}$$

and the formation constant is given by

$$\beta_{1,2,1} = \frac{[VO(2OA)OH.PhOH]_{org}}{[VO(2OA)OH]_{org}\ [PhOH]_{org}}$$

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At higher concentration of the phenol, 1:2:2 adduct is formed

$$VO(2OA)OH.PhOH_{org} + PhOH_{org} \rightleftharpoons VO(2OA)OH.2PhOH_{org}$$

and the formation is given by

$$\beta_{1,2,2} = \frac{[VO(2OA)OH.2PhOH]_{org}}{[VO(2OA)OH.PhOH]_{org}[PhOH]_{org}}$$

The overall reaction can be represented as

$$VO^{+}_{2\,aq} + 2HOA_{org} + 2PhOH_{org} \rightleftharpoons VO(2OA)OH.2PhOH_{org} + H^{+}_{aq}$$

and the extraction constant can be expressed as

$$Kex = \frac{[VO(2OA)OH.2PhOH]_{org}\ [H^{+}]_{aq}}{[VO^{+}_{2}]_{aq}\ [HOA]^{2}_{org}\ [PhOH]^{2}_{org}}$$

The distribution ratio is then given by

$$D_{1,2,2} = \frac{[VO(2OA)OH]_{org} + [VO(2OA)OH,PhOh]_{org} + [VO(2OA)OH.2PhOH]_{org}}{[VO^{+}_{2}]_{aq}}$$

$$\text{or } D_{1,2,2} = \beta_{1,2}[HOA]^{2}_{org}\,(1 + \beta_{1,2,1}[PhOH]_{org} + \beta_{1,2,1}\,\beta_{1,2,2}\,[PhOH]^{2}_{org}).[H^{+}]^{-1}_{aq}$$

The subscript aq, org, HOA and PhOH denote aqueous

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phase, organic phase, hydroxamic acid and phenol respectively.

The distribution ratio, $D_{1,2,2}$ is a function of the concentrations of reagent, phenol and H^+. Thus phenol may be co-ordinated to the VO(2OA)OH complex through the basic V = O group and enhance the distribution coefficient of the metal in the chloroform phase.

4.1.7 <u>APPLICATION OF THE METHOD:</u> The validity of the present method was tested by determining the vanadium content of steel samples. Since the standard steel samples were not available, a synthetic samples were prepared by mixing the constituent metal salts in the same proportion as they are present in British Chemical standard steel No. 64a, 64b, 241/1 and 252. The results of the analysis are given in Table 14.

TABLE 14

DETERMINATION OF VANADIUM IN BCS[a] STEELS

BCS steel No	Vanadium found[b] /	Vanadium added /	Standard deviation
64a	1.56	1.57	± 0.0030
64b	1.97	1.99	± 0.0020
241/1	1.55	1.57	± 0.0028
252	0.45	0.46	± 0.0025

[a] British Chemical Standards, b Average of 5 determinations.

Composition of steel:

64a V, 1.57, Cr, 4.40; Mo, 4.11; W, 5.66/.

64b V, 1.99; Cr, 4.55; Mo, 4.95; W, 7.05/.

241/1 V, 1.57; Cu, 0.1; Si 0.33; Sn, 0.025; P, 0.021;
S, 0.033; Cr, 5.03; Mo, 0.52; W, 19.61; Mn, 0.295;
Co, 5.67; Ni, 0.075/.

252 V, 0.46; Si, 0.24; Mn, 0.016; Ni, 4.10; Cr, 0.20;
Mo, 0.007; Cu, 0.11; Co, 0.04; Sn, 0.004/.

4.1.8 <u>COMPARISON WITH OTHER METHODS:</u> Several reagents have been recommended for the spectrophotometric determination of vanadium (V) (39 - 49, 66 - 78).

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Most of these methods lack selectivity and suffer from the interference by iron and one or more elements such as copper, nicel, 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.

N-phenylbenzohydroxamic acid (46) and its analogues (17 - 20, 27 - 32) have been commonly used as selective reagents for the extractive photometric determination of vanadium (V) in concentrated hydrochloric acid media. However, Ti (IV), Zr (IV), Mo (VI) and W (VI) interfere seriously. It has also been shown by some workers (79,80) that extraction is not quantitative because of the partial reduction of vanadium (V) in concentrated hydrochloric acid media.

A number of drawbacks mentioned above are successfully eliminated in the proposed method. In the presence of p-chlorophenol, the extraction of vanadium (V) is quantitative in dilute hydrochloric acid medium and there is no partial reduction of vanadium (V) (81). The proposed method is highly selective and most of the common ions including Fe(III), Ti (IV), Zr (IV) and Mo (VI) do not interfere. The sensitivity of the method is good and the method is free from the rigid control of experimental conditions. The comparison of

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the present method with the common methods used for the determination of vanadium is summarised in Table 15 and 16.

TABLE 15

SENSITIVITIES OF THE METHODS FOR VANADIUM

Reagent	Colour of complex	λ-max nm	Sensitivity $\mu gVcm^{-2}$	Reference
Hydrogen peroxide	Brown red	450	Varies with acidity	66
Phosphotungstic acid	Yellow	400	0.027	67
Tropolone	Blue	590	0.011	68
3-Hydroxyl-1,3-diphenyltriazine	Yellow green	410	0.0078	69
1-(2-Pyridylazo) 2-naphthol	Blue	615	0.003	72
8-Hydroxyquinoline (chloroform extn)	Magenta black	550	0.016	75
8-Hydroxyquinoline in presence of p-phenylphenol	Blue	620	0.008	52
1,2,3-Phenyloxyamide	Blue violet	560	0.011	48

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Table 15 Con't

Reagent	Colour of complex	λ-max nm	Sensitivity ugVcm^{-2}	Reference
N-hydroxy-N-(m-tolyl)-N-(5-chloro-2-methylphenyl)-p-toluamidinehydrochloride in presence of β-naphthol	Greenish blue	620	0.007	55
Benzo-hydroxamic acid	Red	450	0.014	77,78
N-Phenylbenzohydroxamic acid	Violet	530	0.011	46
N-Phenylcinnamohydroxamic acid	Bluish violet	540	0.008	20
N-Phenylcinnamohydroxamic acid in presence of p-chloro phenol	Bluish violet	565	0.0068	-
N-Phenylcinnamohydroxamic acid in presence of thiocyanate	Green	590	0.0068	-

TABLE 16

SELECTIVITIES OF THE METHODS FOR VANADIUM

Reagent	Acidity	Interference	Reference
Hydrogen peroxide	0.6-6N H_2SO_4	Fe,Cr,Mo,Ti,W	66
Phosphotungstic acid	0.5N	Fe,Cr,Cu,Co, Mo,Sn,Sb,Ti	67
Tropolone	5.5-7.0M HCl	Mn,Br,I	68
3-Hydroxy-1,3-diphenytriazine	3.0-6.0 PH	Fe,Mo,Ti,Cr, Cu	69
1-(2-Pyridylazol)-2-naphthol	3.5-4.5 PH	Fe,Cr,Cu,Mn Co	72
8-Hydroxyquinoline (Chloroform extn)	3.5-4.5	Fe,Cu,Ti	75
8-Hydroxyquinoline in presence of p-phenyl-phenol	2.5-5.0 PH	+	52
1,2,3-Phenyloxyamidine	1.0-10M CH_3COOH	Ti,W	48
N-Hydroxy-N-(m-tolyl)-N' (5-chloro-2-methyl phenyl) p-toluamidine-hydrochloride in presence of β-naphthol	0.00-3.0M CH_3COOH	W +	55
Benzohydroxamic acid	1.2-5.5 PH	Fe,Mn,Al	77,78
N-Phenylbenzohydroxamic acid	5.0-9.0M HCl	Ti,Zr,Mo,W	46

..../..

Table 16 cont'd

Reagent	Acidity	Interference	Reference
N-Phenylcinnamohydroxamic acid	3.0-7.5M HCl	Ti,Mo,W	20
N-Phenylcinnamohydroxamic acid in presence of p-chlorophenol	1.0-3.0M HCl	W	-
N-Phenylcinnamohydroxamic acid in presence of thiocyanate	3.0-7.0M CH_3COOH	Fe,W	-

+Interference of iron is eliminated by using masking agent.

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4.2 VANADIUM (V)-PCHA-SCN MIXED COMPLEX

CHLICE OF SOLVENT FOR EXTRACTION: Several non-polar organic solvents such as chloroform, carbontetrachloride, 1,2-dichlorobenzene, benzene, toluene, xylene and diethylether were found to extract the ternary complex from the aqueous phase. Chloroform was preferred because the reagent is more freely soulble in it than in other solvents and with it the quantitative extraction of the complex is readily accomplished.

4.2.1 ABSORPTION SPECTRA: The absorption spectra of the reagent, vanadium (V)-PCHA complex and vanadium (V)-PCHA-SCN complex in chloroform are shown in Fig. 10. The pink coloured vanadium (V)-PCHA complex has maximum absorption at 510 nm with a molar absorptivity of 4300 $l.mole^{-1}cm^{-1}$. When the vanadium (V)-PCHA complex is extracted in presence of thiocyanate, the colour of the complex changes green and the wavelength of maximum absorption shifts to 590 nm with a consequent increase in molar absorptivity. Thus the formation of mixed ligand complex is accompanied with a hyper and bathochromic

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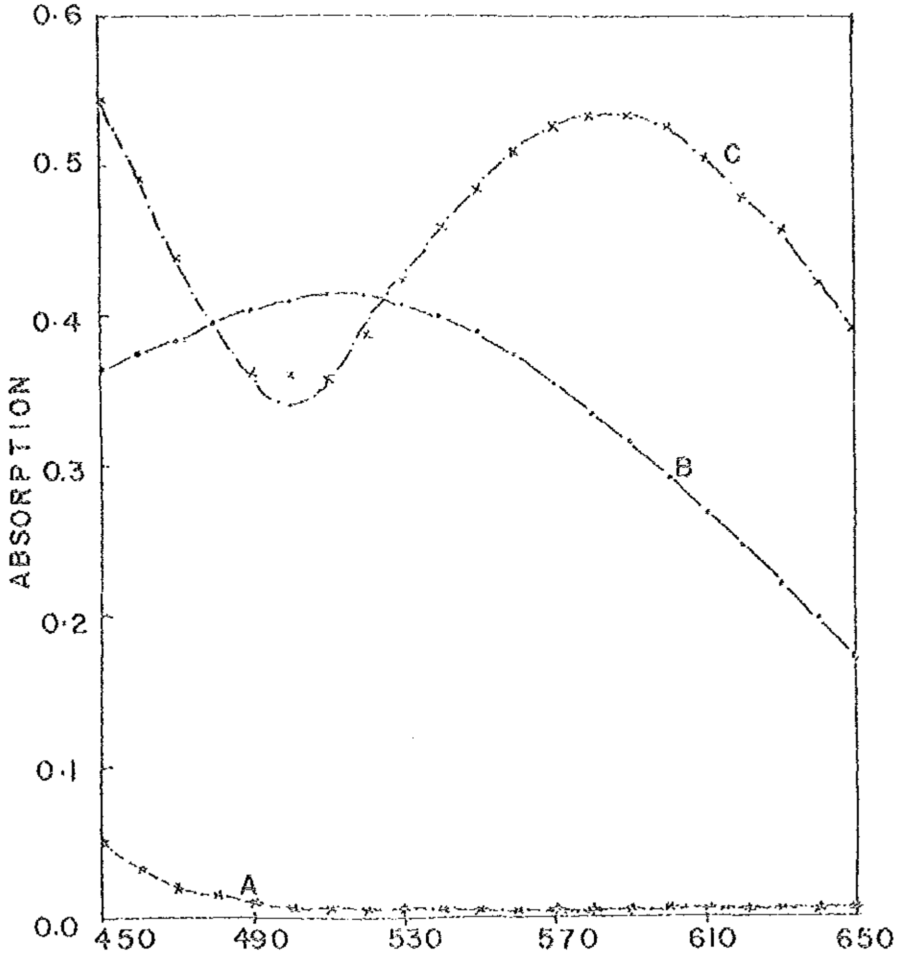

Fig.10 ABSORPTION SPECTRA OF :

A. PCHA ($C_R = 2.00 \times 10^{-3}$ M)

B. VANADIUM(V)-PCHA COMPLEX($C_V = 7{\cdot}07 \times 10^{-5}$ M)

C. VANADIUM(V) -PCHA-SCN COMPLEX
($C_V = 7{\cdot}07 \times 10^{-5}$ M)

shifts.

4.2.2 EFFECT OF VARIABLES: The influence of various experimental parameters on the extraction and determination of vanadium (V) as mixed complex has been studied. The effect of particular variable was investigated by determining vanadium following the recommended procedure described earlier, keeping all the experimental conditions constant except the one under study.

ACIDITY: The optimum acidity range for the extraction and maximum colour intensity was found to be 3.0 to 7.0M with respect to acetic acid (Fig. 11 Table 17). Acetic acid was found to be the best among the common acids employed for extraction of the vanadium complex. Hydrochloric and sulphuric acids are unsuitable for adjusting the acidity of the aqueous phase because the time required for complete extraction varies from 5 to 10 minutes and the complex is unstable.

TABLE 17

EFFECT OF ACETIC ACID CONCENTRATION ON THE EXTRACTION OF VANADIUM - PCHA - SCN MIXED COMPLEX INTO CHLOROFORM

Vanadium concentration = 90µg/25 ml

Concentration of acetic acid in the aqueous phase M	Absorbance at 590 nm
0	0.177
1	0.499
2	0.519
3	0.527
4	0.531
5	0.534
6	0.525
7	0.528
8	0.511
9	turbid

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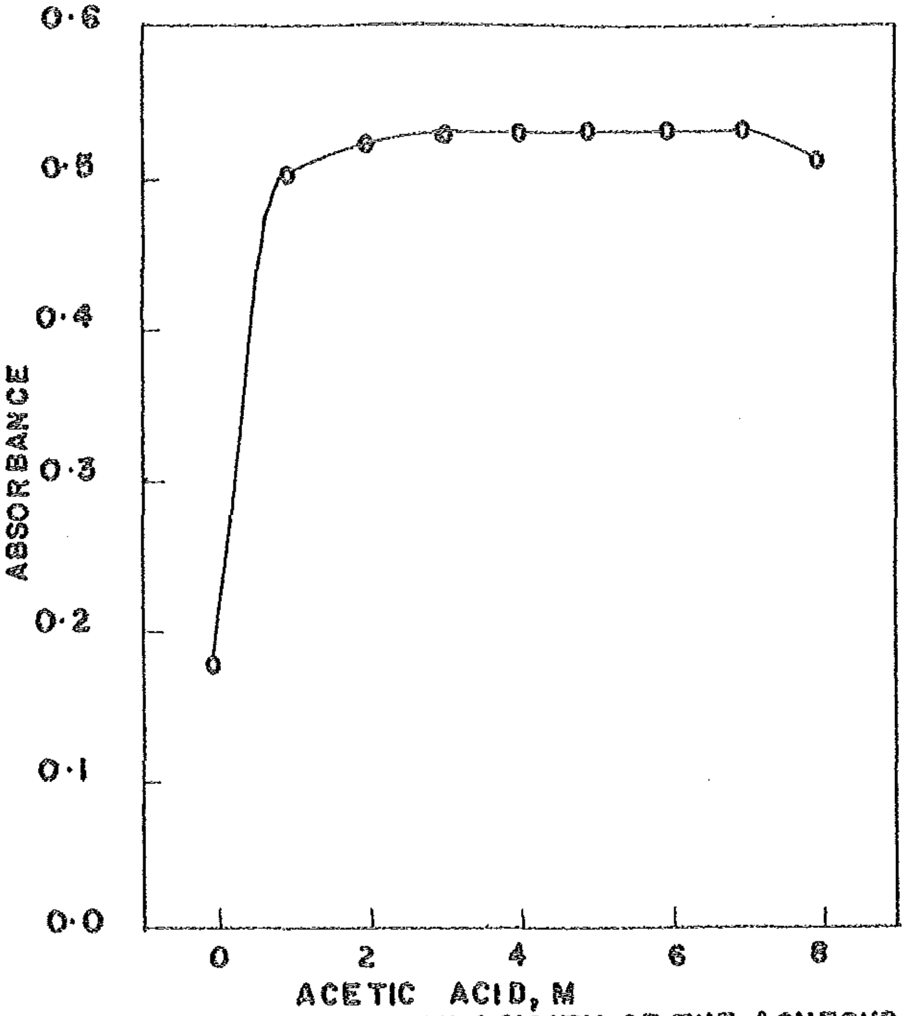

Fig· 11 EFFECT OF ACIDITY OF THE AQUEOUS PHASE· ON EXTRACTION OF VANADIUM-(V)-PCHA-SCN COMPLEX.

Nitric acid is also unsuitable because it oxidizes the reagent; where as both the reagent and the complex extracted from acetic acid medium are stable and the extraction is readily accomplished within 2 minutes.

AMOUNT OF REAGENT (PCHA): A 1:4 molar ratio of vanadium to reagent was found to give maximum colour intensity (Table 12). The reagent and the ternary complex of vanadium have well separated absorption peaks so that excess of the reagent does not interfere in the photometric determination of vanadium.

AMOUNT OF THIOCYANATE: A 300 fold molar excess of thiocyanate was found to be adequate extraction of vanadium (Table 13). A further excess of thiocyanate has no effect on the extraction of vanadium.

ORDER OF ADDITION OF REAGENT: The order of addition of thiocyanate is critical. There is no colour reaction if thiocyanate is added before the extraction of vanadium-PCHA complex in chloroform. Hence, thiocyanate is added after the extraction of pink coloured vanadium-PCHA complex in chloroform.

TIME AND TEMPERATURE: A shaking time of 2 minutes is sufficient for the complete reaction of vanadium-PCHA complex with thiocyanate to form the mixed ligand

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complex. The chloroform extracts are stable for at least 48 hours at 25°C ± 2°C. The absorbance

TABLE 18

STABILITY OF THE EXTRACT

Vanadium concentration = 90µg/25 ml

Acetic acid concentration of the aqueous phase = 4.0M

Time of measurement after extraction minute/hour	Absorbance at 590 nm
0	0.530
0.5	0.532
1	0.529
1.5	0.530
2	0.528
3	0.527
4	0.530
6	0.531
12	0.527
24	0.529
48	0.533

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TABLE 18

EFFECT OF TEMPERATURE OF THE AQUEOUS PHASE

Vanadium concentration = 90µg/25 ml
Acetic acid concentration = 4.0M

Temperature of the aqueous phase °C	Absorbance at 590 nm
20	0.530
25	0.532
30	0.531
35	0.530

TABLE 20

EFFECT OF AMOUNT OF REAGENT (PCHA)

Vanadium concentration in the organic phase = 4.0×10^{-5}M

Acetic acid concentration in the aqueous phase = 3.75M.

Mole ratio of reagent to vanadium	Absorbance at 590 nm
0.4:1	0.065
0.6:1	0.094
0.8:1	0.122
1:1	0.153
1.5:1	0.196
2:1	0.235
3:1	0.275
4:1	0.298
6:1	0.300
8:1	0.302
10:1	0.301
20:1	0.300
50:1	0.302

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TABLE 21

EFFECT OF THIOCYANATE

Vanadium concentration in the aqueous phase = 2.0 X 10^{-4}M.
Acetic acid concentration in the aqueous phase = 4M

Mole ratio of thiocyanate to vanadium	Molar concentration of thiocyanate (in the aqueous phase) M	Absorbance at 590 nm
00:1	0.00	0.345
50:1	0.01	0.390
100:1	0.02	0.436
150:1	0.03	0.481
200:1	0.04	0.527
250:1	0.05	0.566
300:1	0.06	0.603
350:1	0.07	0.602
400:1	0.08	0.602
500:1	0.10	0.600
1000:1	0.20	0.601
2000:1	0.40	0.602
3000:1	0.60	0.604
4000:1	0.80	0.600
5000:1	1.00	0.600

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of the chloroform extracts remains unaltered by variation in temperature of the aqueous phase from 20 to 35°C.

IONIC STRENGTH AND VOLUME OF AQUEUCUS PHASE: The absorption of the coloured system and the extraction of vanadium are not affected by the change in ionic strength of the aqueous phase from 3.0 to 8.0 gram moles per litre with potassium chloride, sodium chloride, ammonium chloride and ammonium nitrate. The volume of the aqueous phase can vary between 10 to 50 ml without affecting the mixed ligand complex formation and its subsequent extraction (Table 22).

4.2.3 **BEER'S LAW, OPTIMUM CONCENTRATION, MOLAR ABSORPTIVITY AND SENSITIVITY:** The coloured system obeys Beer's Law from 0.8 to 6.4 ppm of vanadium (Table 24, Fig. 12). The optimum concentration on the basis of Ringbom's (60) plot (Fig. 13) is 1.5 - 5.0 ppm of vanadium. The molar absorptivity of the ternary complex in chloroform is 7500 litre mole^{-1}cm^{-1} with a photometric sensitivity (61) of 0.0068µg of vanadium per cm^2.

4.2.4 **PRECISION:** The relative standard deviation of the method, calculated from the absorbance values of samples each containing 4 ppm of vanadium is found to be ± 0.55/.

TABLE 22

EFFECT OF IONIC STRENGTH OF THE AQUEOUS PHASE

Vanadium concentration = 90ug/25 ml
Acetic acid concentration of the aqueous phase = 3.0M

Concentration of NaCl M	Absorbance at 590 nm
0.0	0.529
1.0	0.530
2.0	0.528
3.0	0.529
4.0	0.529
5.0	0.530

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TABLE 23

EFFECT OF VOLUME OF THE AQUEOUS PHASE

Vanadium concentration = 90µg/25 ml
Volume of the organic phase = 10 ml

Volume of the aqueous phase ml	Absorbance at 590 nm
05	0.533
10	0.534
20	0.531
30	0.529
40	0.530
50	0.528

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TABLE 24

CALIBRATION CURVE DATA FOR DETERMINATION OF VANADIUM (V)

Concentration of acetic acid in the aqueous phase = 5M

Vanadium µg/25 ml in chloroform	Absorbance at 590 nm
15	0.088
25	0.147
50	0.294
75	0.442
100	0.590
125	0.736
150	0.886
160	0.942

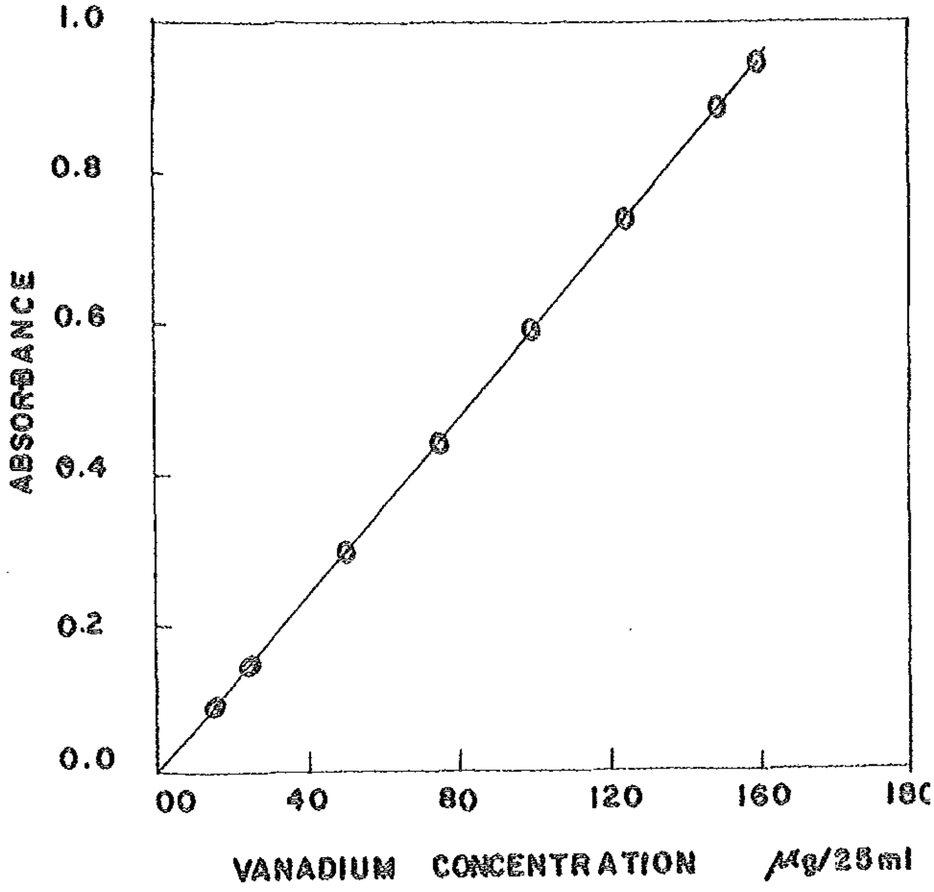
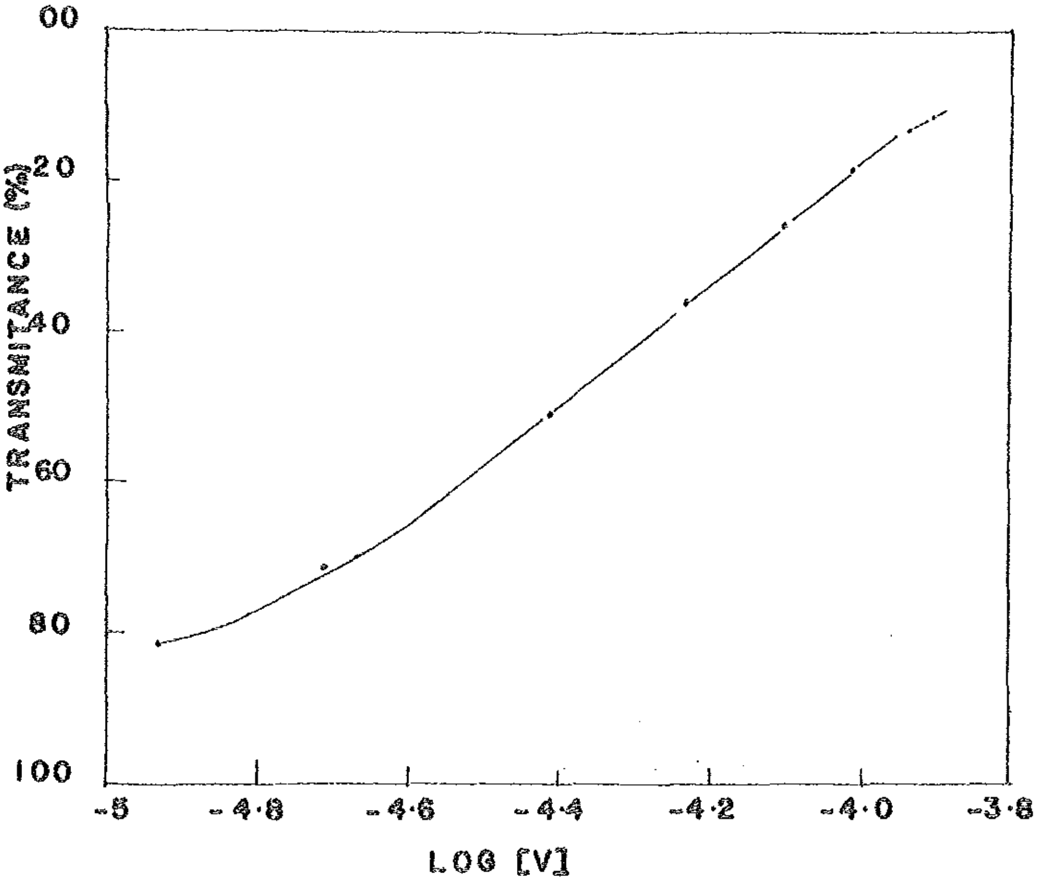


Fig. 12 CALIBRATION CURVE FOR DETERMINATION OF VANADIUM (V)



Fig·13 RINGBOM'S PLOT TO DETERMINE THE EFFECTIVE CONCENTRATION OF VANADIUM (V)·

4.2.5 EFFECT OF DIVERSE IONS: In order to assess possible analytical applications of the reaction, the effect of diverse ions on the extraction and determination of vanadium (V) was studied by adding a known amount of the ion in question to a solution containing 100µg of vanadium and proceeding as in recommended procedure.

Al(III), As(V), Ba(II), Be(II), Bi(III), Ca(II), Cd(II), Ce(IV), CO(II), Cr(III), Cu(II), Ga(III), Hg(II), In(III), La(III), Mg(II), Mn(II), Ni(II), Pb(II), Sn(IV), Sr(II), Sb(V), Th(IV), Tl(I), U(VI), Zn(II), ammonium, acetate, borate, citrate, oxalate, perchlorate, phosphate, sulphate, and tartarate do not interfere with the determination of vanadium even when the weight ratio of each of these ions to vanadium is 200:1. Ti(IV), Zr(IV) and Mo(VI) also do not interfere when the weight ratio of each of these ions to vanadium 50:1.

Fe(III) and W(VI) interfere with the determination of vanadium. Interference due to Fe(III) is a serious drawback of the method, however, it may be eliminated by the use of suitable masking agent.

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4.2.6 COMPOSITION OF THE COMPLEX

The composition of the complex was determined by different methods. The job's (63) and mole ratio (62) methods were employed to determine the ratio of PCHA to vanadium and curve fitting method (64) was employed to determine the ratio of thiocyanate to vanadium. The results obtained indicate the formation of 1:2:2 (V:PCHA: SCN) ternary complex. The experimental details are described below.

<u>JOB'S METHOD OF CONTINUOUS VARIATIONS:</u> The mole fractions of vanadium and PCHA were continuously varied with a constant total molarity by mixing the different volumes of equimolar solutions of vanadium and PCHA. Thiocyanate concentration was kept constant but in excess.

The absorbance of the extracts were measured at 590 nm (Table 25) and plotted against the mole fractions of vanadium (Figure 14). Maximum absorbance occured at a mole fraction of 0.33 ([V]/([V] + [PCHA])) (Fig. 14). This suggests the combining ratio of 1:2 (metal: ligand).

TABLE 25

JOB'S METHOD OF CONTINUOUSVARATIONS

Concentration of vanadium
solution = 1.0 X 10^{-3}M
Concentration of PCHA solution = 1.0 X 10^{-3}M
Concentration of thiocyanate in the
aqueous phase = 0.25M
Concentration of acetic acid in
aqueous phase = 3.75M

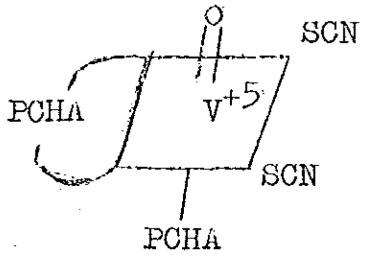
Vanadium Xml	Water (10-x)ml	Reagent (10-x)ml	Chloroform Xml	Absorbance at 590 nm
1	9	9	1	0.300
2	8	8	2	0.589
3	7	7	3	0.826
3.3	6.7	6.7	3.3	0.870
4	6	6	4	0.800
5	5	5	5	0.718
6	4	4	6	0.608
7	3	3	7	0.454
8	2	2	8	0.300
9	1	1	9	0.155

<u>MOLE RATIO METHOD:</u> In this method the molar concentration of vanadium was kept constant and the mole ratio of reagent to vanadium were varied. Again the thiocyanate concentration was kept constant but in excess throughout the experiment.

The subscript aq, org, and HOA denote aqueous phase, organic phase and hydroxamic acid.

Thus the distribution ratio of vanadium is a function of the concentrations of reagent in organic phase and that of thiocyonate in the aqueous phase.

The following structures are proposed:



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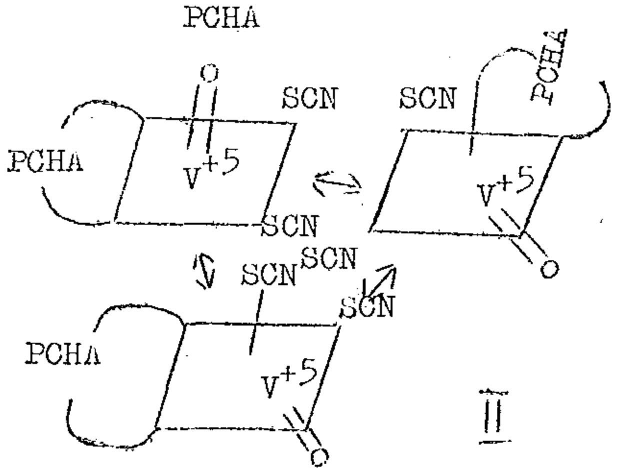

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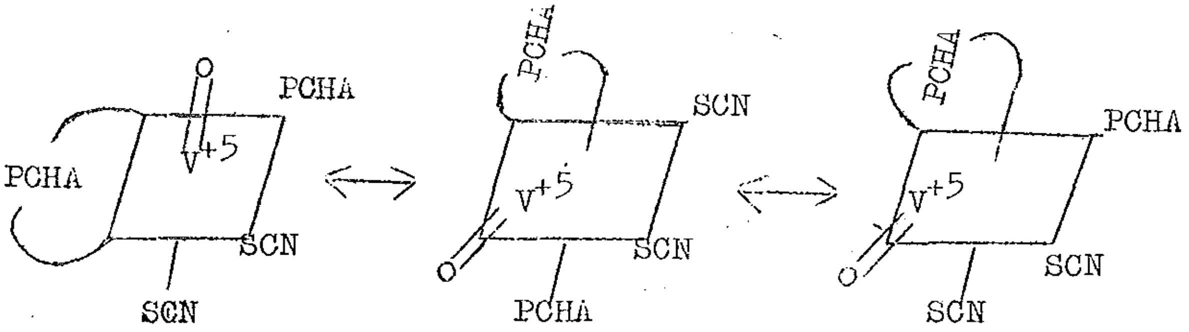
and structure, I, will have the following isomers.



The IUPAC name for structure I is oxodithiocyanatobis-(PCHA)vanadium (V).

.2.7 COMPARISON WITH OTHER METHODS: Among the several reagents recommended for the spectrophotometric determination of vanadium (39), hydrogen peroxide (66), phosphotungstic acid (67), 3-hydroxy-1,3-diphnyltrialine (69,70,71), pyridylazophenols (72-74), tropolone (68) N-hydroxy N-,N-diarylbenzamidines (48,83), benzohydroxamic acid (77,78), N-phenylbenzohydroxamic acid (46), and its analogues (27-30, 39,46,91,92) are in general use.

The comparative study of the proposed method with the other well known method is summarised in Table 15 and 16.

The proposed method is simple, rapid and highly sensitive. Most of the common ions do not interfere, however, the method lacks the selectivity due to the interference of iron which is almost always associated with vanadium in alloys and complex materials. One of the distinct advantage of the present method over the widely used N-phenylbenzohydroxamic acid (46) is the extraction of vanadium from acetic acid medium instead of hydrochloric acid medium in which the extraction is not quantitative due to the partial reduction of vanadium (79,80). It should be noted that most of the common methods used for the determination of vanadium also suffer from the interference of iron and some other metals.

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CONCLUSION

New sensitive and selective methods for the extraction and photometric determination of vanadium (V) with N-phenylcinnamohydroxamic acid have been developed on the basis of synergic extraction and mixed ligand complex formation with p-chlorophenol and thiocyanate. The methods are simple, rapid, precise, accurate and free from the rigid control of experimental conditions. Most of the common ions normaly associated with vanadium in complex materials do not interfere. Both methods are applicable to the analysis of complex materials for vanadium.

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