




**Preparation And Properties of
N-phenylbutyrohydroxamic Acid and
N-p-Chlorophenylbutyrohydroxamic Acid And
Their Uses As Extracting Agents For Chromium
(VI), Molybdenum (VI), Titanium (IV) and
Uranium (VI)**

By

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*A thesis submitted for the degree of Master of Science
in Chemistry*

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Dedication

***To my family
and freinds***

Acknowledgment

*I would like to express my greatfull thanks to
my supervisor Dr.*

*Hassan A/Aziz A/ Alla for his guidance,
great help full and great advices throughout
this work*

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the Chemistry Department University of
Khartoum*

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Abstract

Two ligands, N- phenylbutyrohydroxamic acid (I) , N-p-chlorophenylbutyrohydroxamic acid (II), were prepared by the reaction of butyryl chloride with β - phenyl-hydroxylamine and N-p- chlorophenylhydroxylamine, respectively .

The acids prepared were identified and characterised through their reactions with Vanadium (V) and Iron (III) , their melting points, Infra- red spectra and Nitrogen content.

The extractive properties of these acids towards the metals Cr (VI) , Mo (VI) ,Ti (IV) and U (VI) were examined at different pH values. The percentage of maximum extraction with the two acids was found to be as follows: for Cr (VI) at pH 1 , (100%) for both acids , Mo (VI) at pH 1 (93.75 %) with acid (I) and (73.75%) with acid (II) , Ti (IV) at pH 2 (33.34 %) with acid (I) and (16.67%) with acid (II) and U (VI) at pH 6 (72%) with acid (I) and (76.%) with acid (II).

The metal :ligand complexes ratios were determined by using the continuous variation method, the ratio of the two ligands with the four metals was found to be 1:2.

Finally the suitability of the two acids for spectrophotometric determination of four metals was examined .

CHAPTER ONE

INTRODUCTION

CHAPTER ONE

Introduction

1.1- Analytical Chemistry:

Since 1894⁽¹⁾ analytical chemistry has developed due to the work of W. Ostwald, and its importance still spreads over all domains of science and technology. Historically it has played a vital role in the development of science.

Analytical chemistry⁽²⁾ may be defined as the science and art of determining the composition of materials in terms of the elements or compounds which they contain.

The elemental analysis⁽³⁾ is the analysis of elements contained in a sample, it has two types, organic and inorganic analysis. When a completely unknown sample is presented to an analyst, the first requirement is to know what substances are present, i.e., identification of the constituent of the sample, this is what is known as qualitative⁽⁴⁾ analysis and the quantitative analysis is concerned with the method of determining the relative proportions of the constituents.

The ideal methods⁽⁵⁾ of analysis would involve measurement techniques of such specificity that only the component of interest would give a reaction or response without interference from other component.

There are many types of quantitative methods⁽⁶⁾ of analysis, usually classified according to the nature of final measurements, for example, in gravimetric, the final measurements consist of determination of weight; in colorimetric analysis, the final measurements consist of measuring indirectly the amount of radiant energy that has been absorbed by the sample.

Many techniques⁽⁷⁾ for separating and concentrating the species of interest has been devised. Examples of these techniques are:

Solvent extraction, Chromatography, Ion exchange, Distillation, Precipitation, Complexation, Electro deposition, Masking and others.

1.1.1- Chromatography:

It was first introduced by the Russian botanist Tswett and then given by many workers⁽⁸⁾. It is defined as a separation that achieved by distributing the solute mixture between two phases, a mobile phase and stationary phase. Separation occurs because the molecules of the mixture are adsorbed on a particle surface or adsorbed into particle pores at different rates.

There are many types of chromatography⁽⁹⁾, Liquid-liquid Partition Chromatography (LLPC), Gas Chromatography (GC) and Gas Liquid Chromatography (GLC).

1.1.2- Ion Exchange:

Ion exchange process was noticed for the first time in 1845⁽⁷⁾ during the investigation of ammonia adsorption in soil, then noticed during the softening of hard water.

The ion exchange separation is limited to sample containing ionized or partially ionized solutes, the stationary phase consists of an insoluble but porous resinous material which contain fixed charge carrying groups and mobile counter ions of which

reversibly exchanged for those of solute which carry alike charges, as the mobile phase travels through the system.

There are two types of ion exchangers:

1- Cationic exchangers:



2- Anionic exchangers:



1.2- Solvent Extraction:

The solvent extraction or Liquid-Liquid extraction is based on the distribution of solute between two essentially immiscible solvents. Usually one is an aqueous phase and the other is an organic liquid. Solvent extraction is widely used as separation technique because of its ease, simplicity, speed, selectivity and convenience¹⁰.

1.2.1- Theory of Extraction:

For all phase distributions, the classical phase rule of Gibbs is applied

$$P + V = C + 2$$

$P \equiv$ number of phases.

$V \equiv$ variance or degree of freedom.

$C \equiv$ number of component.

In a particular case of solvent extraction we are dealing with two essentially immiscible solvents and one solute distributed between them so that, $P = 2$, and $C = 3$. At constant temperature and pressure, the rule predicts a variance of unity. This means

that if we choose the concentration of solute in one phase, the solute concentration in the other phase is fixed, hence there will be a definite relationship between the solute concentration in each of the solvent phase. This relation is described in distribution law.

1.2.2- Distribution Law:

The distribution law was first stated in 1872 by Berthelot and Jungfleish⁽¹¹⁾, and then elaborated by Nernst in 1891⁽¹²⁾.

The law states that: at equilibrium, a given solute distributed between two immiscible liquids in the same proportions which can be expressed mathematically as:

$$K_D = [A_{org}] / [A_{aq}]$$

where K_D is the distribution or partition coefficient, A_{org} & A_{aq} are known as the concentrations of solute (A) distributed between immiscible phases provided that its molecular state is the same in both liquids and that the temperature is constant.

$$\text{The distribution ratio } D = [C_A]_{org} / [C_A]_{aq}$$

where C_A is the total concentration of solute A in all its forms, when D is very large only one extraction is enough to remove a substance from the solution, other wise, several extractions are required.

1.2.3- Successive Extractions :

For a given amount of extracting solvents, it is more effective to divide it into several small portions and use each portion successively rather than to make a single extraction with all of the solvent at one time.⁽¹³⁾

For the general case assume that W_o gram of a solute originally present in V_A cm^3 of solvent (A) is to be extracted with successive portions of V_B cm^3 of solvent (B)

$$K_D = C_B / C_A$$

we have $W_o = W_A + W_B$,

$$W_A = C_A V_A,$$

$$W_B = C_B V_B$$

After the first equilibration, fraction in A,

$$\frac{W_{A,1}}{W_o} = \frac{C_{A,1} V_A}{C_{A,1} V_A + C_{B,1} V_B}$$

$$\frac{W_{A,1}}{W_o} = \frac{V_A}{V_A + \frac{C_{B,1} V_B}{C_{A,1}}}$$

$$= \frac{V_A}{V_A + K_D V_B}$$

$$W_{A,1} = W_o \frac{V_A}{V_A + K_D V_B}$$

For the second extraction,

$$\begin{aligned} W_{A,2} &= W_{A,1} \frac{V_A}{V_A + K_D V_B} \\ &= W_o \frac{V_A}{V_A + K_D V_B} \end{aligned}$$

Repeating procedure for n- equilibrations gives:-

$$W_{A, n} = W_o \left(\frac{V_A}{V_A + K_D V_B} \right)^n$$

1. 2. 4. Separation Of Mixtures By Extraction :-

The great value of extraction is the possibility of separating two or more substances based upon a difference in their distribution co-efficient. If one solute has (k) much greater than one and the other much less than one, a single extraction will cause nearly complete separation, this arise only when two solute are very different chemically, if the two solute have similar but not identical distribution coefficient, a single extraction will cause only partial separation with an enrichment at of one solute in one solvent and an enrichment of the other solute in the other solvent. The effectiveness of separation is usually expressed by means of separation factor, (β) ,⁽¹³⁾

$$\beta, = \{[A]_{org} / [A]_{aq}\} / \{[B]_{org} / [B]_{aq}\} = D_A / D_B$$

where $[A]_{org}$, $[B]_{org}$, $[A]_{aq}$ & $[B]_{aq}$ are the concentration of solute (A) and (B) in organic and aqueous layers respectively.

1.2.5- Extraction Efficiency:

The efficiency of extraction depends on the magnitude of (D) and on the relative volumes of liquid phases. The percentage extracted (% E) is given by

$$\% E = 100 \{W_{org} / (W_{org} + W_{aq})\}$$

% E can be expressed in term of concentration (C) and volume (V).

$$\% E = 100 \{ C_{org} V_{org} / (C_{org} V_{org} + C_{aq} V_{aq}) \}$$

Dividing by $C_{aq} V_{org}$, then the equation becomes:

$$\% E = 100 D / \{ D + (V_{aq} / V_{org}) \}$$

If $V_{aq} = V_{org}$, then

$$\% E = 100D / (D + 1)$$

1.2.6- Types of Extraction:

a) Batch Extraction:

Is the simplest and most useful method, it is employed when a large distribution ratio of the desired separation exists. In this method, the two layers are shaken in a separatory funnel until equilibrium is obtained.

b) Continuous extraction:

Is used when distribution ratio is very small. This method, makes use of a continuous flow of immiscible solvent through the solution. The efficiency of this method depends on the distribution ratio and the viscosity of the two phases.

c) Discontinuous Counter Current Distribution Extraction:

This method was devised by Craig in 1973, in which multiple extractions could be done rapidly in sequence. This method is applied mainly to substances with similar distribution ratio.

1.2.7- Advantages of solvent extraction:

Lyman⁽¹⁴⁾ stated these advantages as:

- 1- Ease and speed of accomplishment due to selectivity.
- 2- General applicability due to fast amount of complexing agents solvent and mixed solvent available.
- 3- The ultimate overall selectivity which can be obtained.
- 4- Reproducibility regardless of different solute proportions or presence of extraneous materials.
- 5- The apparatus are simple and cheap.
- 6- Number of solutes can be isolated simultaneously.
- 7- The amount of sample required is governed by the purity required or the concentration factor desired, both of which can easily be calculated.

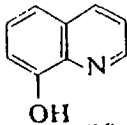
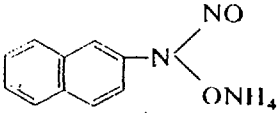
1.2.8- Stripping (Back Extraction):

Is the removal of extracted solute from the organic phase for more preparation for detailed analysis. Since most analysis are still carried out in aqueous phase at the end of extraction process, the removal of solvent by distillation or evaporation has been widely provided if the solvent is volatile. If the extract is equilibrated with an aqueous solution at pH unfavourable to the formation of the extracted species, the chelate can be destroyed and the metal ion extracted back into the aqueous phase.

1.3- Organic Analytical Reagents:

Organic reagents were first used in analytical chemistry by M A. Linsky (1856) and L. A. Chugaev (1873)⁽¹⁵⁾.

Analytical organic reagents have been used in gravimetric, volumetric and spectrophotometric analysis, they are also used in column chromatography and thin layer chromatography for elution and detection.

Typical examples are; 8-hydroxyquinoline () used to separate aluminium from alkali and alkaline earth metals⁽¹⁶⁾, N-benzophenyl-hydroxylamine suggested by Shome⁽¹⁷⁾ as a precipitating agent for Cu (II), Fe (III) and Ti (IV). Also Cupferron⁽¹⁸⁾ () is one of the best known organic reagents which form extractable chelates with many metals. The extraction of cupferrates of 33 metals with chloroform was studied in relation to the pH value.

All metals can be determined colorometrically by use of organic reagents. The organic reagents which form a five or a six membered ring with the cations by donation of electron-pairs, are called chelating agents such as dimethylglyoxime $\text{CH}_3\text{-C=NOH}$
 $\text{CH}_3\text{-C=NOH}$

For analytical application, reagents are usually chosen so that acidic and basic groups are in such position as to form five or six membered chelate rings. There is no known specific reagent, however, by right choice of masking agent conditioning of the reaction environment, the reactions which a reagent can participate can be made very selective or even specific.

Selectivity of the reaction often increases as the functional group which forms the chelates through two oxygen atoms can be changed to those chelating through one

oxygen and one nitrogen atom. Even greater selectivity is expected when the electronegativity of the coordinating atom is increased and also such electronegative group may increase the acidity and thus makes the reagent more effective as a complexes formed therefore are less stable⁽¹⁹⁾. Steric govern the stability of the chelate and hence the selectivity of the reaction.

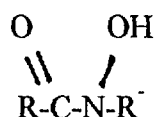
Dimethylglyoxime (2, 3-dioximinobutane)* is a weak dibasic acid, used in gravimetry for Nickel (II) and Palladium (II). In contrast to this reagent, 8-hydroxyquinoline, under the correct condition, precipitate almost any metal apart from those in group 1A. To precipitate selectively, just one metal, it is necessary to control the pH and use complexing reagent such as Cyanide ions or EDTA, to hold another ion in solution. Diphenylcarbazide (1, 5-diphenylcarbazide) $[\text{CO}(\text{NH.NHC}_6\text{H}_5)_2]$, this reagent in acid solution of chromates gives a soluble violet compound.

1.4- Hydroxamic Acids:

1.4.1- Introduction:

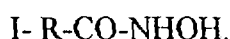
In 1869⁽²⁰⁾, H. Lossen reported that the reaction between diethyloxalate and hydroxylamine yielded an acidic compound which he named Oxalohydroxamic acid. Later, H. Lossen found that benzoyl chloride and hydroxyl ammonium chloride gave a mixture of benzohydroxamic acid, benzoylbenzohydroxamate and dibenzohydroxamic acid.

Hydroxamic acids have a general formula:



where R & R' are hydrogen, alkyl or aryl group, therefore, a large number of derivatives are available with different R & R' group.

Hydroxamic acids exist in solutions as equilibrium mixture of the two tautomers⁽²¹⁾:



where (I) is hydroxyamide or hydroxamic acid and (II) is hydroxyimine or hydroxamic acid. When an acyl⁽²²⁾ group replaces one of the nitrogen bonded hydrogen in hydroxylamine molecule, a monohydroxamic acid, R-CO-NHOH, is formed and when another hydrogen of hydroxylamine is substituted by an aryl⁽²³⁾ group, the N-arylhydroxamic acid formed. They are prepared by the reaction of N-arylhydroxylamine with acid chloride.

1.4.2- Nomenclature of Hydroxamic acid:

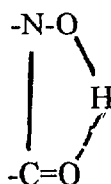
Hydroxamic acid are derivatives of carboxylic acids, thus the nomenclature system is based on the naming of these carboxylic acids. In naming specific compound, the practice is drop the (-ic) of the related carboxylic acid and substitute the letter (O), followed by hydroxamic acids⁽²⁴⁾.

1.4.3- Properties of Hydroxamic acids:

Hydroxamic acids are in general, colourless somewhat low melting point solids⁽²⁵⁾. The N-arylhydroxamic acids⁽²⁶⁾, are white or pale yellow crystals, sparingly soluble in water and n-hexane, soluble in benzene and chloroform.

Hydroxamic acid are very weak acids, however, they are several times stronger than phenols⁽²⁷⁾. The pKa value vary from 7.05 for nitrobenzohydroxamic acid to 11.33 for N-phenylbutryl hydroxamic acid⁽²⁸⁾.

The acidity of hydroxamic acid⁽²⁹⁾ may be attributed essentially to the inductive effect of the (O-H) hydroxyl group and the suppression of the basic character of the central nitrogen due to its conjugation with acyl group. Suppression of acidic character may be attributed to intramolecular hydrogen bonding



1.4.4.- Characterization Of hydroxamic acids:

Hydroxamic acids give characteristic colours with certain metal ions. They give violet colour with Vanadium (V) and red violet colour with ferric solution. Chloroform solution of hydroxamic acid gives violet extract with Vanadium (V) from concentrated hydrochloric acid medium, also gives a violet red colour with Iron (III) depending on the pH⁽³¹⁾.

The Infra Red Spectra⁽³²⁾ of hydroxamic acids show the most characteristic bands associated with their functional grouping. The value of characteristic bands are due to (OH) at 3200, (C=O) at 1600 and (N-O) at 910 cm^{-1} stretching bands.

The Ultra-Violet Spectra⁽³³⁾ have only been determined for arylhydroxamic acids and their N-substituted and O-substituted derivatives.

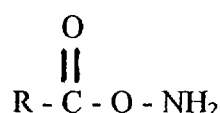
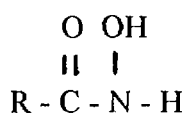
Many reactions⁽³⁴⁾ characteristic to $\begin{smallmatrix} \text{O} & \text{OH} \\ \parallel & | \\ \text{R}-\text{C} & -\text{N}- \end{smallmatrix}$ functional group were known. The oxidation of hydroxamic⁽³⁵⁾ acids (via) their radical anion

$\begin{smallmatrix} \text{O} \\ | \\ \text{R}-\text{C}-\text{N}^{\cdot}-\text{O}^- \end{smallmatrix}$ gives N-o-Diacyl-hydroxylamines $\text{R}-\text{CO}-\text{NH}-\text{O}-\text{COR}$, by many oxidants like periodic acid, bromine, mercuric oxide and potassium ferricyanide. Also oxidation of N-alkyl hydroxamic acids gives N-alkyl-NO-diacyl hydroxylamines together with oximes or their oxidation products.

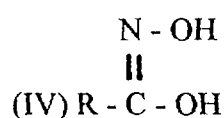
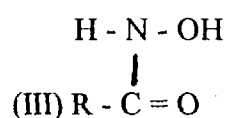
1.4.5. Structure of Hydroxamic Acids:

Hydroxamic acids exist⁽³⁶⁾ in two forms,

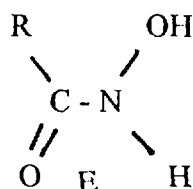
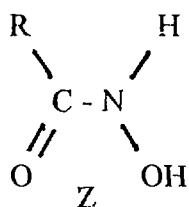
(I) N-acyl derivative and (II) O-acyl derivatives



N-acyl are found in two tautomeric forms, keto-and enol-forms (III) and (IV) respectively.



If there is restricted rotation⁽³⁷⁾ about C - N bond, the Z and E isomers of the keto form exist, as do the enole form.



The calculations show that the Z-keto isomers become the more stable due to H-bonding.

The crystals are stabilized by a network of intermolecular hydrogen bonds.

Bond distance and bond angles as well as conformational parameters of hydroxamic acids have been analyzed⁽³⁸⁾.

1.4.6 Preparation of Hydroxamic Acid:

Hydroxamic acids have been prepared by different methods, the most common two are; the reaction between acid chloride and hydroxylamine, and the other between esters and hydroxylamine.

1- The reaction between an ester and hydroxylamine:

An alkyl or aryl ester^(39, 40) reacts with hydroxylamine in the presence of alkali, the free acid obtained by acidification of cold solution. this reaction takes place in an absolute alcohol and proceeds rapidly at room temperature particularly in presence of an equimolar quantity of sodium alkoxide⁽⁴¹⁾. Dutta⁽⁴²⁾ used sodium methoxide instead of potassium hydroxide in preparing nictino hydroxamic acid.

2- The reaction between acid chloride and hydroxylamine:

In this reaction the N-substituted^(43, 44) hydroxylamine is acylated by acid chloride to produce a monohydroxamic acid, a derivative which is undesired is also produced. Tandon⁽⁴⁵⁾ improved this method by using equimolar proportion of N-substituted hydroxylamine and acid chloride at low temperature diethyl ether medium containing aqueous suspension of sodium hydrogen carbonate.

There are many methods which are less common for preparation of hydroxamic acids:

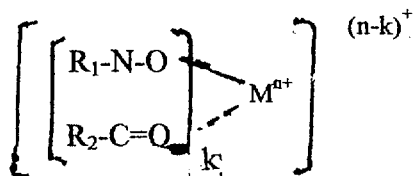
The reaction between carboxylic acid and hydroxylamine in presence of Ni (II) as a catalyst⁽⁴⁶⁾. Acetohydroxamic acid was prepared through catalysis with Nickel⁽⁴⁷⁾.

The reaction between acid anhydride and amides⁽⁴⁸⁾ with hydroxylamine.

The reductive rearrangement of oximinoester⁽⁴⁹⁾. Also the oxidation of aldoximes, amines, aldehydes ammonias, amides and nitriles by Carro's reagent ($\text{H}_2\text{S}_2\text{O}_8$)⁽⁵⁰⁾.

1.4.7- Metal Complexes of hydroxamic acids:

Hydroxamic acids have an extraordinary complexing⁽⁵¹⁾ ability towards a very great number of metal ions because they have bidentate group. The complex formation between a metal M^{n+} and hydroxamic acid usually takes place with the replacement of the hydroxylamine hydrogen by the metal ion and ring closure through the carbon-oxygen to form the chelate⁽⁵²⁾.



The ketoform of hydroxamic acid contain one easily replaceable proton (mono basic) while enol form may dissociate two protons, thus behaving as a di basic acid.

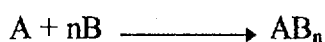
The Keto - enol totmerism provides anumber of sites which are avialable for metal ion coordination. The hydroxamic acid⁵³ group behaves as a typical bidentate donor towards various metal ions, generally hydroxamic acids form salts nearly with all the elements of group I, II, III and lanthanides and actinides group of the periodic

Table. For example, N-phenylbutyrohydroxamic acids⁽⁵⁴⁾ form a divalent metal chelates with Cu (II), Ni (II), Zn (II) and Mn (II) in a metal to ligand value of 1:2 for determination of the formula of these complexes a method of continuous variation methods is used.

1.4.8- Continuous Variation Method:

This method was worked out by Denison⁽⁵⁵⁾ in connection with his studies of compound formation in liquid mixture. Later it was applied by Job⁽⁵⁷⁾ to the spectrophotometric determination of the formulae of the complexes formed in solutions by reaction of two components.

The formation⁽⁵⁶⁾ of many complex ions can be represented by equation:



where A is a metallic ion, B may be either ion or molecule. To determine n, solutions of A and B of the same molar concentration are mixed in varying proportion and a suitable property of resulting solutions is measured. The monochromatic light is a suitable property for this method. The absorption of light is proportional to the concentration of absorbing species which is one of the necessary conditions. The absorbance of each solution is measured and is then plotted against the mole fraction of the ligand (A/ A+B), Triangular shaped curve is obtained. The ratio of the metal : ligand is determined from the curve where the maximum absorbance is obtained.

1.4.9- Biological Activities of Hydroxamic Acids:

Hydroxamic acids are useful in biology⁽⁵⁸⁾ and medicine⁽⁵⁹⁾ fields. Recent progress⁽⁶⁰⁾ in hydroxamic acid chemistry has been stimulated by the isolation of

several naturally occurring and the synthesis of a number of medicinally active hydroxylamine derivatives. A few recent examples will now be considered a series of o-, m- and p-alkoxybenzohydroxamic acid were found to be highly effective against pathogenic fungi, while salicyhydroxamic acids and derivatives are effective antibacterial and antifungal agents. β -alkylaminopropanohydroxamic acid shows hypotensive properties and a number of hydroxamic acids and N-hydroxy ureas possess hypocholesteremic activity, P-butoxy phenyl aceto hydroxamic acid (bufexamac) is in actual use as an anti-inflammatory agent in human. A series of terephthalohydroxamic acids and other dicarbohydroxamic acids have been investigated as potential antimalarials.

Hydroxamic acids⁽⁶¹⁾ are also known as constituent of growth factors, food additives, antibiotics, antibiotic antagonists, tumor inhibitors, antifungal agents and cell division factors, several of them have been used as drugs. They are also potent and specific inhibitors of ureas activity, thermolysin, elastase and aminopeptidases. These enzymes are metalloproteinases and the mechanism of inhibition appears to involve chelation of metals at their active site.

1.4.10- Analytical Application of Hydroxamic Acids:

Hydroxamic acids^(61, 62) have received considerable attention as reagents in analytical chemistry for gravimetric analysis and for solvent extraction and spectrophotometric determination of metals.

N-benzophenylhydroxylamine⁽⁶³⁾ was introduced as gravimetric reagent by Shome (1950), has been one of the most useful reagents to appear in recent years. It

has been used extensively for determination of many metals. The thio- analogue, thiobenzohydroxamic acid forms chelates of generally greater stability.

In 1959, Shome⁽⁶⁴⁾ determined spectrophotometrically the red compound formed by Vanadium with benzophenylhydroxamic acid, the coloured compound formed in presence of ethanol at pH 2.5 shows maximum absorbance at 480 nm. Also (B.P.H.A) used for determination of Cu, Fe and Al gravimetrically, later it was used by Agrawal⁽⁶⁵⁾ for determination of Cd, the optimum pH for complete precipitation is 5.8 - 6.5, the complex formula $(C_{13}H_{10}NO_2)_2Cd$.

N-acetylsalicyloyl-N-phenylhydroxylamine⁽⁶⁵⁾ used by Joseph and Savarior for determination of Ti (IV) spectrophotometrically and gravimetrically. Spectrophotometrically is highly selective, the deep yellow colour shows maximum absorbance at 390 nm. In gravimetry, the yellow precipitate formed in 1-2 M HCl can be weighed directly after drying at 105°-115°C.

Agrawal in 1973⁽⁶⁷⁾ determined U (VI) spectrophotometrically at pH 4.0-4.5 in 0.1 M N-phenyl-2-naphthohydroxamic acid in chloroform, the absorption maximum at 515 nm. And in 1975⁽⁶⁸⁾ he extracted U (VI) with N-m-tolyl-o-methoxybenzohydroxamic acid, the complex was extracted into chloroform at pH 5.3-5.5, a maximum absorption of orange red extract occur at 510 nm. In 1977⁽⁶⁹⁾, Agrawal used N-m-tolyl-m-nitrobenzohydroxamic acid to determine U (VI) gravimetrically. The precipitate was carried out at pH 4.5 - 5.6 and was dried at 110°C as $(C_{14}H_{11}N_2O_4)_2UO_2$.

In 1978⁽⁷⁰⁾, Caupta and Chandravanshi used N-p-chlorophenyl-p-methoxy benzohydroxamic acid. as a sensitive reagent for Ce (IV) at 450 nm. Agrawal and

Roshania⁽⁷¹⁾ used N-p-chlorocinnamohydroxamic acid for gravimetric determination of Be, Mg, Ca and Ba by adjustment of pH, the precipitates were dried at 110°C and weighed as $M(C_{15}H_{11}O_2Cl)_2$.

In 1964, Majumdar⁽⁷²⁾ and Das showed that N-benzoyl-o-tolylhydroxamic acid form reddish-violet complex with V (V) which can be extracted in chloroform and has an absorption maximum at 510 nm.

N-m-tolyl-p-methoxy benzohydroxamic acid. was prepared by Gupta and Tandon⁽⁷³⁾ and used for extraction of V (V) in 4 M HCl. The interference was caused by Mo, Ti & Zr. Fe (III), Cu (II) & U (VI) do not interfere up to ratio of 2000 ppm or greater.

In 1980⁽⁷⁴⁾, V (V) was determined spectrophotometrically by Koshy and Tandon with N-p-chlorophenyl-2-naphthohydroxamic acid. The violet complex was extracted from 3 - 8.4 M HCl.

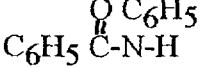
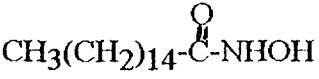
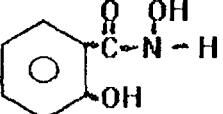
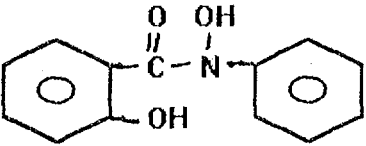
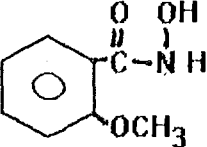
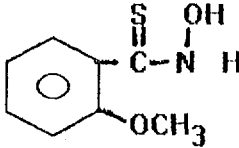
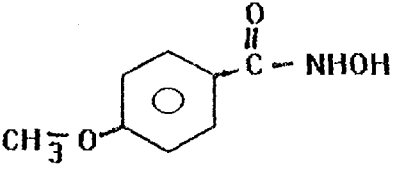
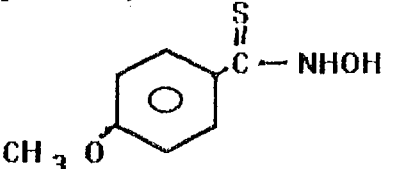
In 1987⁽⁷⁵⁾, Basant and Tandon used N-benzyl-2-naphthohydroxamic acid for determination of V (V) from 4-5 M HCl, the reddish-violet extract shows maximum absorption at 505 nm.

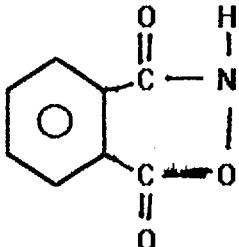
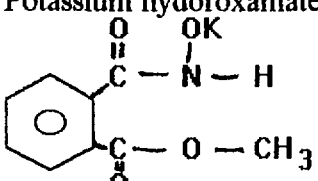
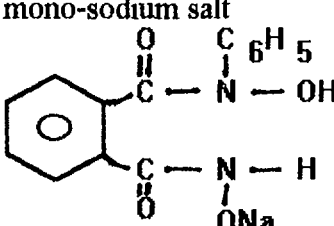
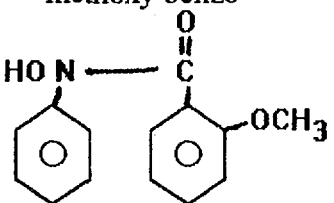
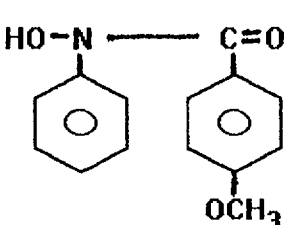
In 1979⁽⁷⁶⁾, Agrawal and Gandbe used N-p-tolyl-o-methoxy benzohydroxamic acid. in iso-amyl alcohol for determination of Mo (VI) which was extracted at pH 2.5-3.5, the yellow extract has λ_{max} at 355.

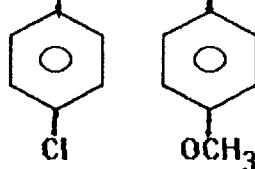
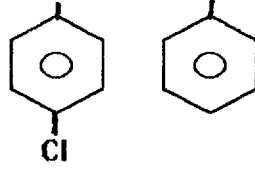
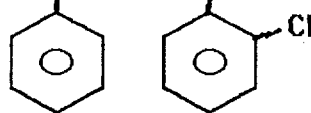
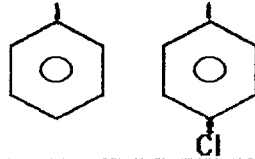
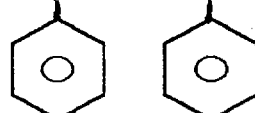
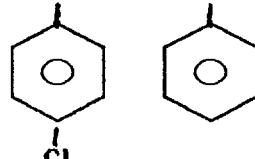
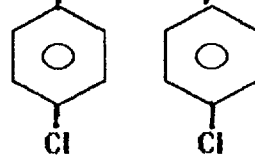
1.4.11 Applications of Hydroxamic Acids Prepared in the Chemistry Department :

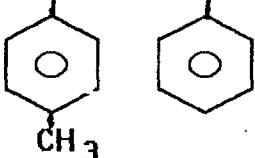
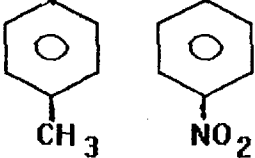
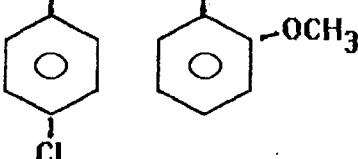
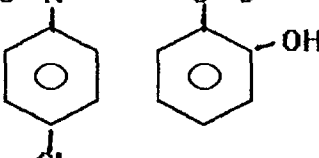
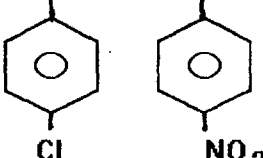
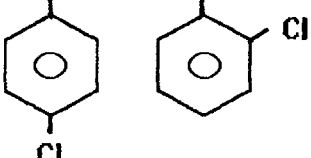
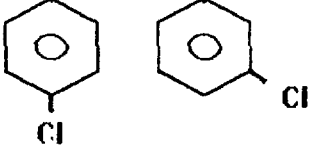
Reagents :

| - hydroxamic acid | Medium (pH) | Metals Extracted | Percentage of Extraction | Reference |
|--|-------------|--|--------------------------|-----------|
| Cotton Seed Oil- | 2 | V ⁵⁺ | 93.0 | 77 |
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_{15}\text{H}_{31}\text{C}-\text{NHOH} \\ + \\ \text{O} \\ \parallel \\ \text{C}_{17}\text{H}_{33}\text{C}-\text{NHOH} \\ + \\ \text{O} \\ \parallel \\ \text{C}_{17}\text{H}_{31}\text{C}-\text{NHOH} \end{array}$ | 5.5 | Fe ³⁺ | 100.0 | |
| | 6 | Ni ²⁺ | 25.5 | |
| | 6.5 | Cu ²⁺ | 89.7 | |
| | 7 | Zn ²⁺ | 11.11 | |
| Sesame seed oil- | 2 | V ⁵⁺ | 86.5 | |
| | 5.5 | Fe ³⁺ | 100.0 | |
| $\begin{array}{c} \text{O} \\ \parallel \\ \text{C}_{15}\text{H}_{31}\text{C}-\text{NHOH} \\ + \\ \text{O} \\ \parallel \\ \text{C}_{17}\text{H}_{33}\text{C}-\text{NHOH} \\ + \\ \text{O} \\ \parallel \\ \text{C}_{17}\text{H}_{31}\text{C}-\text{NHOH} \end{array}$ | 6 | Ni ²⁺ | 27.7 | |
| | 6.5 | Cu ²⁺ | 91.0 | |
| | 7 | Zn ²⁺ | 21.0 | |
| Stearo- | 5&7,1,1 | Ti ⁴⁺ , V ⁵⁺ , Mo ⁶⁺ | 74,28,41.5 | 78 |
| $\begin{array}{c} \text{H}-\text{N}-\text{OH} \\ \\ \text{C}_{17}\text{H}_{35}\text{C}=\text{O} \end{array}$ | 6,7,6 | Fe ³⁺ , Ni ²⁺ , Cu ²⁺ | 80,3.6,75 | |
| N-Phenyl Stearo- | 7,7 | Zn ²⁺ , U ⁶⁺ | 2.4,74.3 | |
| $\begin{array}{c} \text{H}-\text{N}-\text{OH} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{OH} \\ \\ \text{C}_{17}\text{H}_{35}\text{C}=\text{O} \end{array}$ | 6,1,1 | Ti ⁴⁺ , V ⁵⁺ , Mo ⁶⁺ | 89,66.2,42.5 | |
| | 5-7,6,6 | Fe ³⁺ , Ni ²⁺ , Cu ²⁺ | 96.8,4.2,88. | |
| | 7,6 | Zn ²⁺ , U ⁶⁺ | 6 | |
| Oleo- | 5-7,1,1 | Ti ⁴⁺ , V ⁵⁺ , Mo ⁶⁺ | 8.2,93.5 | |
| $\begin{array}{c} \text{H}-\text{N}-\text{OH} \\ \\ \text{C}_{17}\text{H}_{33}\text{C}=\text{O} \end{array}$ | 4,527,5 | Fe ³⁺ , Ni ²⁺ , Cu ²⁺ | 93.7,76,96.2 | |
| | 5-7,7 | Zn ²⁺ , U ⁶⁺ | 90.3.5,85 | |
| N-Phenylleo- | 5,1,1 | Ti ⁴⁺ , V ⁵⁺ , Mo ⁶⁺ | 7,90 | |
| $\begin{array}{c} \text{H}-\text{N}-\text{OH} \\ \\ \text{C}_6\text{H}_5-\text{N}-\text{OH} \\ \\ \text{C}_{17}\text{H}_{33}\text{C}=\text{O} \end{array}$ | 5,7,6 | Fe ³⁺ , Ni ²⁺ , Cu ²⁺ | 78,29.2,73.2 | |
| | 7,6 | Zn ²⁺ , U ⁶⁺ | 97.6,4.2,94 | |
| | | | 18.4,84.5 | |

| -hydroxamic acid | Medium (pH) | Metals Extracted | Percentage of Extraction | Ref |
|--|-----------------------------|---|--|-----|
| N-Phenyl benzo-  | 5,3,6 | Cu^{2+} Fe^{3+} , Zn^{2+} , | 93,91,56.5 | 79 |
| C_6H_5 $\text{C}-\text{N}-\text{H}$ | 6,6 | Ni^{2+} , Mn^{2+} | 52,29 | |
| Palmito-  | 6,6,6 | Cu^{2+} Fe^{3+} , Zn^{2+} , | 80,82,20 | |
| $\text{CH}_3(\text{CH}_2)_{14}-\text{C}-\text{NHOH}$ | 6,6 | Ni^{2+} , Mn^{2+} | 23,10 | |
| Salicyl-  | 6,6,5 5,1,9 7,4 | Fe^{3+} Ni^{2+} Ti^{4+} U^{6+} Mo^{6+} Cd^{2+} Cu^{2+} V^{5+} | 99.5,7.0,71.4 92.5,99.5,11 100,98 | 80 |
| N-Phenyl Salicyl-  | 2,6,1 5,8,2 8,6,3,8 | Fe^{3+} Ni^{2+} Ti^{4+} U^{6+} Zn^{2+} Mo^{6+} Cd^{2+} Cu^{2+} V^{5+} Co^{2+} | 100,13,83 57,10.5,92 14.5,100,100,8.5 | |
| o-Methoxy-benzo  | 6,6,4 5,2,6 3,9 | Fe^{3+} Ni^{2+} Ti^{4+} U^{6+} Mo^{6+} Cu^{2+} V^{5+} Co^{2+} | 99,10.5,88.8 77,98,97 100,13 | |
| o-Methoxy benzo thio-  | 6,5,1 5,8,6 1-7,3,5,8 | Fe^{3+} Ni^{2+} Ti^{4+} U^{6+} Zn^{2+} Mo^{6+} Cu^{2+} V^{5+} Co^{2+} Cd^{2+} | 98,97,67.6 95.5,100,100 100,100,97,100 | |
| p-methoxy benzo  | 7 7 | Cu^{2+} Mo^{6+} | 91.4 95.1 | 81 |
| p-Methoxy benzo thio-  | 5,7,2-4 4,3 | Cu^{2+} Zn^{2+} Ag^{1+} Au^{3+} Mo^{6+} | 99.5,99.4,99.5 95.5,95.1 | |

| | | | | |
|---|--|---|---|-----------|
| <p>Amino phthalic anhydride</p>  | <p>2,2 6,6 6,6</p> | <p>$V^{5+} Mo^{6+} Cu^{2+}$ $Fe^{3+} Cd^{2+} U^{6+}$</p> | <p>75,60 47,89 36,1,97</p> | <p>82</p> |
| <p>Mono methyl Phthalate-2-Potassium hydroxamate.</p>  | <p>2,2 6,6 6,6</p> | <p>$V^{5+} Mo^{6+} Cu^{2+}$ $Fe^{3+} Cd^{2+} U^{6+}$</p> | <p>51.25,60 45.62,88.4 46,51.87</p> | |
| <p>N-phenyl/di-hydroxamate mono-sodium salt</p>  | <p>2,2 6,6 5,6</p> | <p>$V^{5+} Mo^{6+} Cu^{2+}$ $Fe^{3+} Cd^{2+} U^{6+}$</p> | <p>60,50 48.3,48 35.6. 45.13</p> | |
| <p>Cotton Seed -(1M)</p> <p>$C_{15}H_{31}C(=O)NHOH$ + $C_{17}H_{33}C(=O)NHOH$ + $C_{17}H_{31}C(=O)NHOH$</p> | <p>M/nitric acid 0.5,4 0.1,0.1</p> | <p>$Mo^{6+} Ti^{4+}$ $U^{6+} Zr^{4+}$</p> | <p>99.4,65.37 35.33,100</p> | <p>83</p> |
| <p>1- N-phenyl-o - methoxy benzo-</p>  <p>2- N-phenyl-p - methoxy benzo-</p>  | <p>7 1 7 1</p> | <p>U^{6+} V^{5+} U^{6+} V^{5+}</p> | <p>100 96.25 100 97.50</p> | <p>84</p> |

| | | | | |
|--|---|--|---|----|
| <p>3- N- p-Cl-phenyl- p-methoxy benzo</p> <p>HO-N — C=O</p>  | 8 1 | U ⁶⁺ V ⁵⁺ | 100 100 | |
| <p>N-p-Cl-Phenyl-N-benzo</p> <p>HO-N — C=O</p>  <p>N-Phenyl-N-o-Cl-benzo-</p> <p>HO-N — C=O</p>  <p>N-Phenyl-N-p-Cl-benzo-</p> <p>HO-N — C=O</p>  | 6 1 7 1 7 1 | U ⁶⁺ V ⁵⁺ U ⁶⁺ V ⁵⁺ U ⁶⁺ V ⁵⁺ | 73.8 100 85 100 95.4 100 | 85 |
| <p>1- N-Phenyl-N-benzo-</p> <p>HO-N — C=O</p>  <p>2- N-p-Cl-Phenyl-N-benzo-</p> <p>HO-N — C=O</p>  <p>3- N-p-Cl-Phenyl-N-p-Cl-benzo-</p> <p>HO-N — C=O</p>  | <p>5,3 M H₂SO₄ 5,1</p> <p>5,3 MH₂O₄ 5,2</p> <p>5,3MH₂O₄ 5,2</p> | <p>Ti⁴⁺ Cr⁶⁺ Fe³⁺ Mo⁶⁺</p> <p>Ti⁴⁺ Cr⁶⁺ Fe³⁺ Mo⁶⁺</p> <p>Ti⁴⁺ Cr⁶⁺ Fe³⁺ Mo⁶⁺</p> | <p>21.7,77.5 87.5,94.25</p> <p>14,57,5 70,90</p> <p>10,57.5 47.5,83</p> | 86 |

| | | | | |
|---|----------------------------------|---|------------------------------|----|
| <p>1- N-p-tolyl-N-benzo-</p> $\text{HO}-\text{N} \xrightarrow{\quad} \text{C}=\text{O}$  | 1,7 6,1 | Mo^{6+} U^{6+} Ti^{4+} Cr^{6+} | 95.40,100 15.48,78.32 | 87 |
| <p>2- N-p-tolyl-N-p-nitro benzo-</p> $\text{HO}-\text{N} \xrightarrow{\quad} \text{C}=\text{O}$  | 1,8 5,8,1 | Mo^{6+} U^{6+} Ti^{4+} Cr^{6+} | 94.68,100 11.16,52.93 | |
| <p>N-p-Cl-Phenyl-o-Methoxy benzo-</p> $\text{HO}-\text{N} \xrightarrow{\quad} \text{C}=\text{O}$  | 3M,1 2,3 3 | Cr^{6+} Mo^{6+} Ti^{4+} Fe^{3+} V^{5+} | 100,92 26.6,97.2 100 | 88 |
| <p>N-p-Cl-Phenyl Salicylo-</p> $\text{HO}-\text{N} \xrightarrow{\quad} \text{C}=\text{O}$  | 1,2& 3M,1 2,5 &6 1, 2,3M&1 | Cr^{6+} Mo^{6+} Ti^{4+} Fe^{3+} V^{5+} | 100,96.2 28,100 100 | |
| <p>N-p-Cl-Phenyl-p-nitro benzo-</p> $\text{HO}-\text{N} \xrightarrow{\quad} \text{C}=\text{O}$  | 3M,1 5,3.6 3 | Cr^{6+} Mo^{6+} Ti^{4+} Fe^{3+} V^{5+} | 99.5,93.6 40.5,100 100 | |
| <p>N-p-Cl-Pheny-o-Cl-benzo</p> $\text{HO}-\text{N} \xrightarrow{\quad} \text{C}=\text{O}$  | 3M,1 5&6,(3-5) 2-3 | Cr^{6+} Mo^{6+} Ti^{4+} Fe^{3+} V^{5+} | 100,91.8 24,100 100 | |
| <p>N-p-Cl-Phenyl-m-chloro benzo-</p> $\text{HO}-\text{N} \xrightarrow{\quad} \text{C}=\text{O}$  | 3M,1M 6,6 1,2,3M,&1-3 | Cr^{6+} Mo^{6+} Ti^{4+} Fe^{3+} V^{5+} | 79,96.7 38,100 100 | |

The aim of the work :-

The aim of this work is to prepare N- phenylbutyro-hydroxamic acid and N-p-chloro phenylbutyro hydroxamic acid , identified them and study their extractive ability towards the transition metals Cr (VI) , Ti (IV) , Mo (VI) & U(VI). As well as the ratio of their compination with the ligands and suitability of them for spectrophotometric determination of four metals which develop colour complexes.

CHAPTER TWO
EXPERIMENTAL
&
RESULTS

CHAPTER TWO

EXPERIMENTAL AND RESULTS

Instruments Used:

1. Jenway pH-meter, Model 3030.
2. Mettler, melting point determination apparatus.
3. U V.-Vis. spectrophotometer, Perkin Elmer 550s.
4. I.R. Spectrophotometer, Perkin Elmer

2.1- Preparation of Hydroxamic Acids:

Reagents:

Nitrobenzene A. R.

P-chloronitrobenzene, A.R.,

Ammonium chloride, A. R. (H. W.),

Sodium chloride, A. R. (B. D. H.),

Zinc dust, G.P.R. (B. D. H.),

n-Butyric acid, G.P.R. (H.W.),

Thionyl chloride, A. R. (H. W.)

Sodium hydrogen carbonate, A.R. (H. W.),

Petroleum ether, A.R. (H.W.),

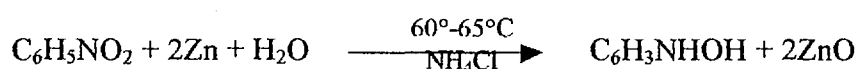
Benzene, A.R. (H.W.).

2.1.1- Preparation of N-phenylbutyrohydroxamic Acid:

a) Preparation of β -phenylhydroxylamine:

Procedure:

In a two liter beaker equipped with a thermometer and mechanical stirrer, 41.6 cm³ (0.4 mole) of nitrobenzene, 25 g of ammonium chloride were mixed up in 800 cm³ of distilled water at 60°C, the mixture was stirred vigorously, 59.5 g (0.9 moles) of zinc dust were added during about 15 minutes, the rate of addition was controlled by the rate of increase of temperature. The temperature raised to 60°-65°C and kept in this range until all zinc had been added. The stirring continued for 15 minutes, by which time the reaction completed as shown by the fact that, temperature commenced to fall. The reaction mixture was filtered to remove the zinc oxide and was washed by 100 cm³ of hot water. The filtrate was placed in a conical flask saturated with sodium chloride and was cooled in an ice bath for one hour to ensure the maximum crystallization of the product. The pale yellow crystals were filtered, yield 34 g (68%)⁽⁸⁹⁾, the product β -phenylhydroxylamine was formed according to the equation:



b) Preparation of Butyryl Chloride:

A reflux condenser was fitted into the short neck of 100 cm³, Claisen flask, separatory funnel into the long neck and the side arm was plugged with a small cork. 37.5 g (22.5 cm³) of n-butyric acid in separatory funnel.

The flask was heated gently on the water bath and n-butyric acid was added during the course of 30-40 minutes, the hydrogen chloride evolved, was absorbed in

water. When all the acid had been introduced, the mixture was heated on water bath for 30 minutes, the apparatus was rearranged and distillation was carried out. The crude acid chloride boiling between 70-110°C was collected in a distilling flask, finally, redistilled from Claisen flask. The n-butyryl chloride was collected at 100-101°C, yield 23 g.⁽⁸⁹⁾

The acid chloride was prepared as follows:

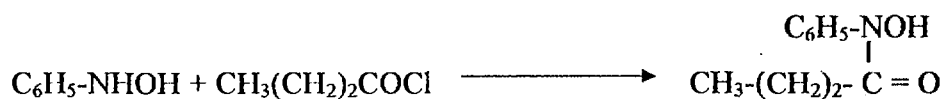


c) The coupling reaction between β-phenylhydroxylamine and butyryl chloride:

0.1 mole (10.9 g) of freshly prepared β-phenylhydroxylamine as prepared in (2.1.1.a) was dissolved in 50 cm³ of benzene in 250-round bottomed flask, a little suspension of sodium hydrogen carbonate in 5 cm³ of water was added, the mixture was stirred vigorously using a mechanical stirrer, 0.1 mole (10.6g) of butyryl chloride was dissolved in 10 cm³ of benzene, placed in a separatory funnel and was added gradually to the mixture in the flask, during this the water was kept alkaline to litmus paper by regular addition of sodium hydrogen carbonate in small amount (about 10g required in all).

Towards the completion of the reaction the colour of the mixture changed from yellow to pink as butyryl chloride was added, on vigorous stirring the colour become yellow again. The time required to complete the reaction was 2.5 hours. The benzene layer evaporated and crystals obtained were recrystallized from a mixture of benzene petroleum ether which gave a white-yellow crystals. The product was dried and weighed, yield 11.0g (61.4%). the melting point was found 80.5°C, (lit 81°C).⁽⁹⁰⁾

The ligand was prepared according to the equation:

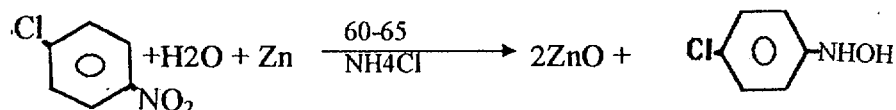


N-phenyl-butyrohydroxamic acid.

2.1.2- Preparation of N-p-chlorophenylbutyrohydroxamic Acid:

a) Preparation of p-chlorophenylbutyrohydroxylamine:

It was prepared by procedure (2.1.1a) except that 63 g of p-chloronitrobenzene were used instead of nitrobenzene according to equation:

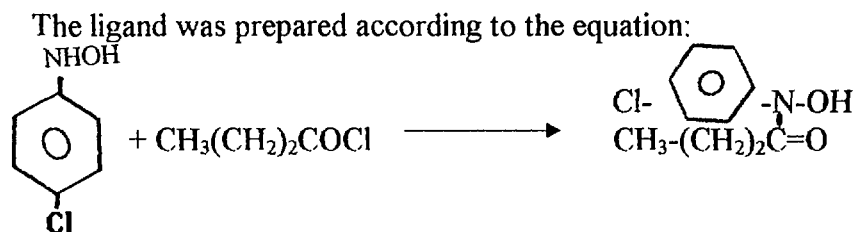


b) Preparation of Butyryl Chloride:

It was prepared by procedure (2.1.1.b).

c) The coupling reaction between p-chlorophenylhydroxylamine and butyryl chloride:

It was prepared by procedure (2.1.1.c) except that p-chlorophenylhydroxylamine was used instead of β-phenylhydroxylamine.



2.2- Determination of The Nitrogen Content of The Hydroxamic Acids

Prepared:

Reagents:

Conc. Sulphuric acid, A. R. (B.D.H.).

Manganese dioxide, A. R.(H.W).

Sodium sulphate, A.R. (B.D.H).

Sodium Hydroxide, A.R. (B.D.H).

Hydrochloric acid, A.R. (B.D.H).

2.2.1-Determination of Nitrogen Content of N-phenylbutyrohydroxamic Acid:

0.5413g of N-phenyl butyrohydroxamic acid was taken in Kjeldhahl flask, 20 cm³ of concentrated sulphuric acid, 3.5g of sodium sulphate and 0.1692g manganese dioxide were added to flask. The mixture was digested on heating mantle in fume chamber till the organic matter destroyed and the solution was clear, the content was cooled and diluted with 50 cm³ water, then, a few antipumping granules were added and a drop of S.M.O indicator. The excess acid was neutralized with 4 M.NaOH, then excess caustic soda was added. 100 cm³ of 0.08 M HCl was placed in the receiver flask which adjusted so that the tip of condenser just dipped in the acid solution. The content was heated to boil gently until 2/3 of original solution distilled off. The excess acid was titrated with 0.13 M. Standard NaOH, the volume of sodium hydroxide which neutralized the excess acid was equal to 39.5 cm³.

$$\text{Nitrogen\%} = \frac{(M_a \times V_a) - (M_b \times V_b)}{\text{weight of sample}} \times 14 \times 100$$

$$= \frac{\{ (M_a \times V_a) - (M_b \times V_b) \} 1.4}{\text{weight of sample}}$$

Where V_a & M_a volume and molarity of standard HCl; V_b & M_b volume and molarity of standard NaOH.

$$\text{Nitrogen\%} = \frac{\{ (100 \times 0.08) - (39.5 \times 0.13) \} 1.4}{0.5413} = 7.40 \%$$

The theoretical value = 7.82 %

2.2.2- Determination of Nitrogen Content N-p-Chlorophenyl-N-

butyrohydroxamic acid:

0.4701g of N-p-Chlorophenyl-N-butyrohydroxamic acid was treated as in (2.2.1). The volume of sodium hydroxide which neutralized the excess acid = 76.50 cm^3 .

$$\text{Nitrogen \%} = \frac{\{ (100 \times 0.09) - (76.5 \times 0.09) \} 1.4}{0.4701} = 6.31$$

Theoretical value = $14 \times 100 / 213.5 = 6.55$.

2.2.3- Determination of Chlorine Content of p-Cl-phenylbutyrohydroxamic Acid:

0.4513g of the acid was cautiously fused with one gram of sodium metal in small pyrex tube on a gentle flame in fume chamber. The fusion continued for along time to make sure that all the excess sodium metal was evaporated, the tube and content were heated strongly to redness, then transferred to a small beaker containing 50 cm^3 of distilled water, using watch glass for protection. The tube was broken

down, the beaker and its content were boiled and filtered, the filter paper was washed with hot water till it is free of chlorine.

The filtrate was acidified with 1 cm³ of conc. nitric acid, 0.1 M silver nitrate solution was added slowly with constant stirring, the precipitate was then allowed to settle down and then few drops of silver nitrate solution were added, if there is no further precipitate, then a slight excess was added. The content was then heated nearly to boiling with constant stirring until the precipitate coagulated and supernatant liquid was clear. 2-3 drops of silver nitrate was added to ensure complete precipitation of silver chloride, then, the beaker and its contents were set in dark for one hour before filtration, then filtered in a pre-weighed and dried filtering crucible, the precipitate in the crucible was washed with very dilute nitric acid until it is free from excess silver nitrate i.e. 3-5 cm³ of washings give no turbidity with 1 or 2 drops of 0.1 M HCl. The crucible and contents were dried at 130-150°C for one hour allowed to cool and weighed.

The weight of silver chloride was found to be 0.305g. Then the weight of chlorine 0.075g. The percentage of chlorine was found to be 16.73 %, theoretical 16.62.

Solvent Extraction

2.3- Preparation of Buffer Solutions:

Reagents:

Hydrochloric acid, A.R. (B.D.H)

Potassium chloride, A.R. (B.D.H)

Acetic acid, A.R. (B.D.H)

Sodium acetate, A.R. (B. D.H)

Ammonium chloride, A.R. (H.W)

Ammonium Hydroxide, A. R.(B. D. H)

Sodium hydroxide, G.P. R (B.D.H)

pH 1 and pH 2 were prepared from a mixture of 0.2 M HCl and 0.2 M KCl in different proportions, and then adjusted by the use of pH meter. Series of buffer solutions ranging from pH 3 to pH 10 were prepared as follows:

Solutions of pH 3, 4, 5 and 6 were prepared using 0.2 M acetic acid and 0.2 M sodium acetate in different proportions. Solutions of pH 8, 9 and 10 were prepared by mixing different volumes of 0.1 M aqueous ammonia and 0.1 M ammonium chloride, all buffers were adjusted to their pH with the pH meter using a few drops of 0.1 M HCl or 0.1 M NaOH according to the need.

2.4- Extraction of Chromium (VI):

2.4.1- Preparation of Chromium (VI) Stock Solution:

1000 ppm Cr (VI) solution was prepared by dissolving 2.823g of potassium dichromate $K_2Cr_2O_7$ in distilled water, transferred quantitatively to 1000 cm³ volumetric flask and completed to the mark with distilled water.

Reagents:

1- 20 ppm of Cr (VI) solution.

2- 10 ppm of Cr (VI) solution.

3- 1 % (W/V) ethanolic solution of diphenylcarbazide.

4- Buffer solution of pH 1-6.

5- 0.02 M of N-phenyl-butyrohydroxamic acid.

2.4.2- Preparation of Standard Calibration Curve:

A calibration curve was prepared by transferring 0.05, 1, 1.5, 2 and 2.5 cm³ of 10 ppm Cr (IV) solution in 25 cm³ volumetric flask, then 5.0 cm³ of 1.0 M H₂SO₄ was added and 1.0 cm³ of 1.0 % of ethanolic solution of diphenylcarbazide was introduced, the solution was completed to 25 cm³ with distilled water, left for few minutes for complete colour development, the absorbance was read at 540 . The result were recorded in Table (1), the absorbance was plotted against the concentration as shown in fig. (1).

2.4.3- Extraction of Cr (VI) With N-phenyl-butyrohydroxamic Acid:

5.0 cm³ of 20 ppm Cr (VI) solution were pipetted into a series of six, 100 separatory funnels, 5.0 cm³ of buffers from pH 1-6 were added to each, then, 10 cm³ of 0.02 M N-phenyl-butyrohydroxamic acid were introduced, the contents were shaking gently for two minutes, the two layers were allowed to separate and the aqueous layers were kept for further analysis.

2.4.4- Determination of Cr (VI) In Aqueous Layers By Di-phenylcarbazide

Method:

1.0 cm³ from each aqueous layer separated in (2.4.3) was taken in 25 cm³ volumetric flask. 5.0 cm³ of 1.0 M H₂SO₄ were added and then 1.0 cm³ of 1.0 % ethanolic solution of diphenylcarbazide was introduced. The solution was completed to the mark with distilled water and left for five minutes for complete colour development. The absorbance was read at 540 nm using 1.0 cm cell and the result

were recorded in Table (2). The amount of chromium in the aqueous layer was calculated from the calibration curve obtained by plotting absorbance against concentration of prepared solution.

2.4.5- Extraction of Cr (VI) With N-p-Cl-phenyl-butyrohydroxamic Acid:

The same procedure followed in (2.4.3) was applied except the using N-p-Cl-phenyl-butyrohydroxamic acid instead of N-phenyl-butyrohydroxamic acid.

2.4.6- Determination of Cr (VI) In The Aqueous Layers:

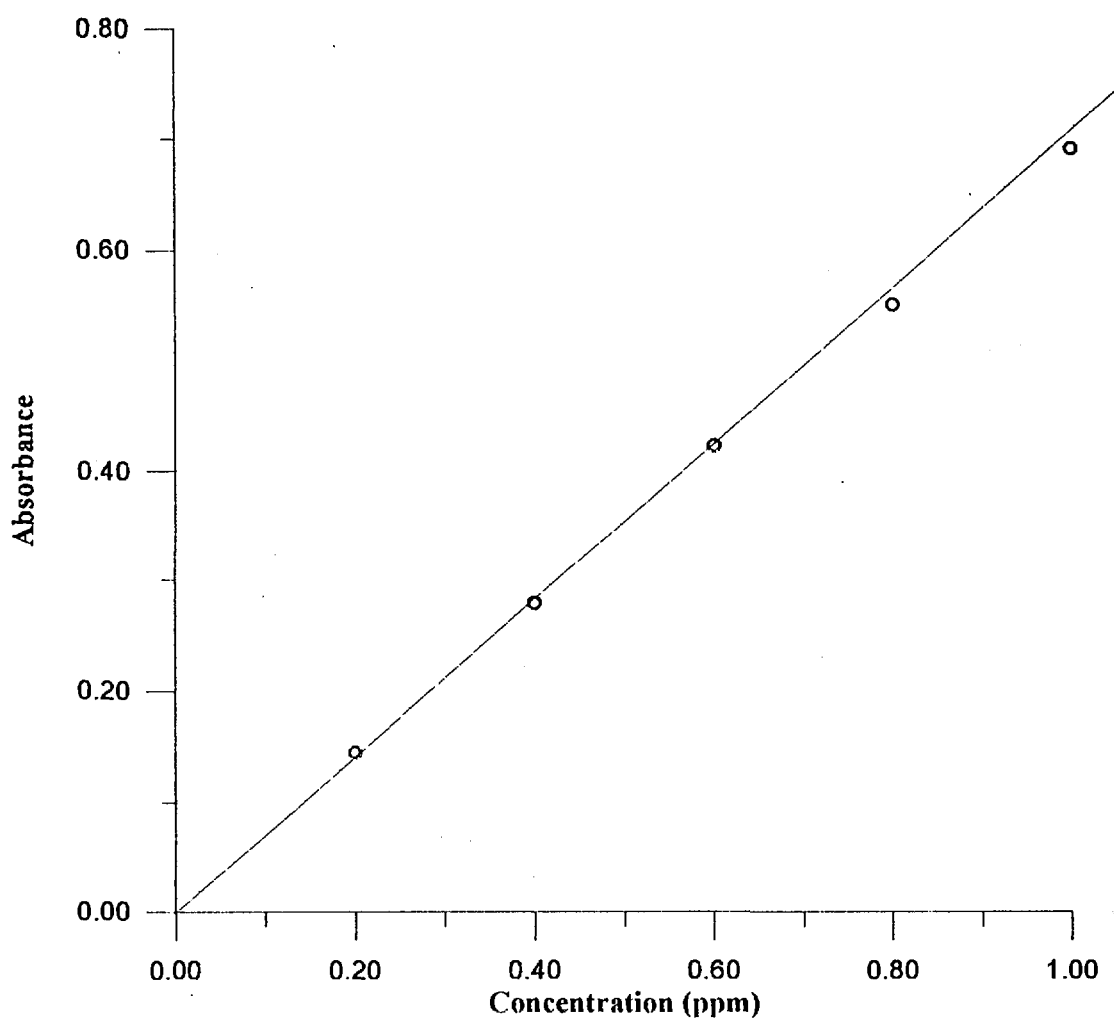
The same procedure as that followed in (2.4.4.). The absorbance was read at 540 nm using 1.0 cm cells. The result were recorded in Table (3).

Table (1): Standard Calibration Readings For Cr (IV):

| Conc. in ppm | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|--------------|-------|-------|-------|-------|-------|
| Absorbance | 0.138 | 0.278 | 0.420 | 0.552 | 0.690 |

Table (2): Results of Extraction of Cr (VI) With N-phenyl-butyrohydroxamic Acid:

| pH | Absorbance | % Remain | % Extracted |
|----|------------|----------|-------------|
| 1 | 0.004 | 0.00 | 100.00 |
| 2 | 0.053 | 17.50 | 82.50 |
| 3 | 0.082 | 27.50 | 72.50 |
| 4 | 0.090 | 32.50 | 67.50 |
| 5 | 0.097 | 35.00 | 65.00 |
| 6 | 0.107 | 37.50 | 62.50 |



**Fig. (1): Standard Calibration Curve For Cr (VI)
With Diphenylcarbazide**

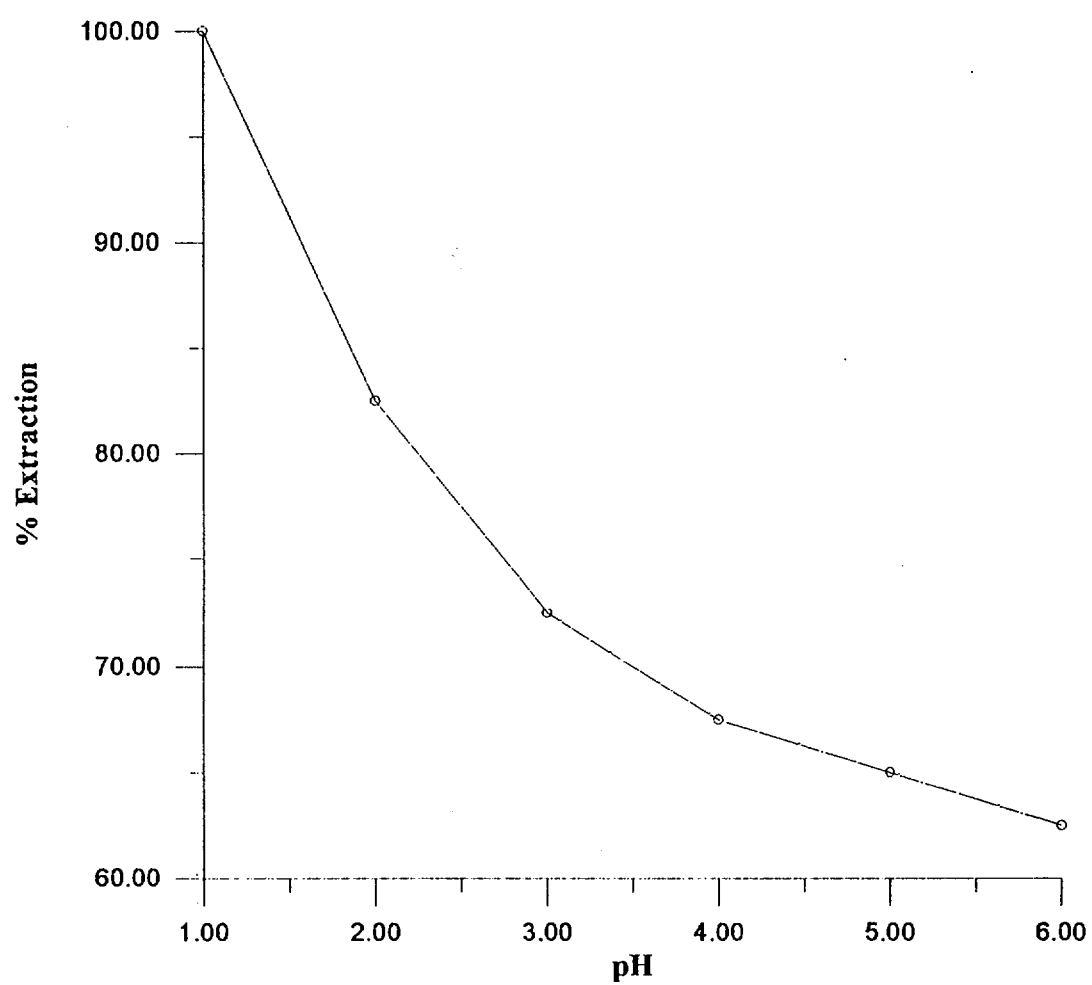


Fig.(2): % Extraction Of Cr (VI) With N-phenylbutyrohydroxamic Acid

Table (3): Results of Extraction of Cr (VI) With N-p-Cl-phenylbutyrohydroxamic Acid:

| pH | Absorbance | % Remain | % Extracted |
|----|------------|----------|-------------|
| 1 | 0.003 | 0.00 | 100.00 |
| 2 | 0.045 | 15.00 | 85.00 |
| 3 | 0.059 | 20.50 | 79.50 |
| 4 | 0.064 | 22.50 | 77.50 |
| 5 | 0.073 | 25.00 | 75.00 |
| 6 | 0.089 | 30.00 | 70.00 |

2.4.7- Determination of The Ratio of Cr :HA Complex Using Continuos

Variation Method:

A series of extractions were carried out in which the mole fraction of Cr (VI) with N-phenylbutyrohydroxamic acid and N-p-chlorophenylbutyrohydroxamic acid were varied from 0.1 to 0.8 respectively. The absorbance of organic extract was measured against the solvent chloroform as a blank at max. 540 nm. Results were recorded in Table (4) and (5).

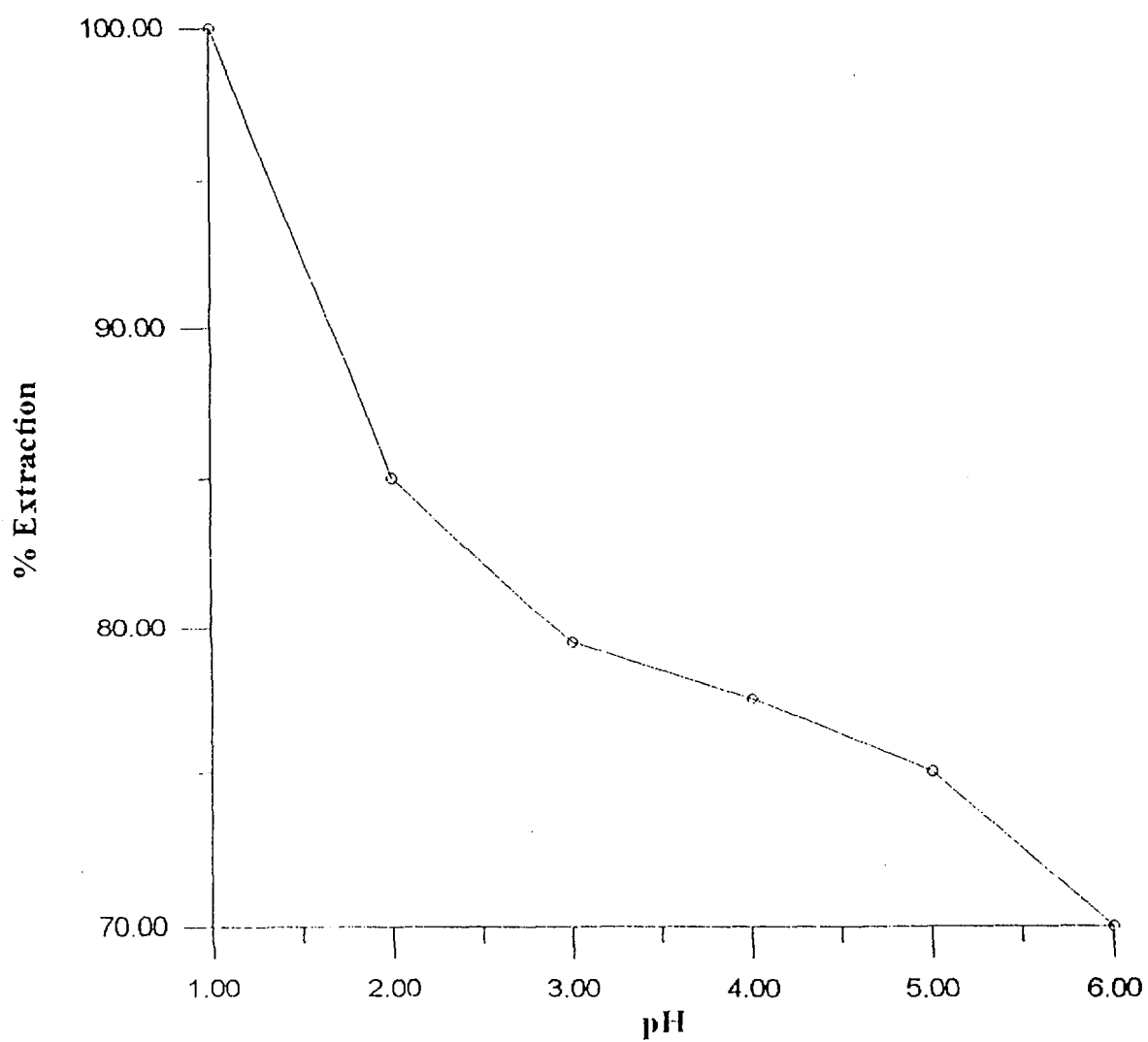


Fig. (3): % Extraction Of Cr (VI) With N-p-Cl-phenylbutyrohydroxamic Acid

**Readings of the ratios of Cr(VI):
Table (4): N-Phenylbutyro H.A complexes,**

| Solution | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|-------|-------|-------|-------|-------|-------|-------|-------|
| Vol. of (0.01) Cr (VI) in cm ³ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Vol. Of pH 1 in cm ³ | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Vol. of dist. water in cm ³ | 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 |
| Vol. of (0.01) H.A in cm ³ | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 |
| Vol. Chloroform added to H.A before added to M ^{tn} | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
| mole fraction M/M+L | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
| Absorbance | 0.045 | 0.057 | 0.072 | 0.065 | 0.058 | 0.049 | 0.040 | 0.031 |

Table (5): Readings of the ratios of Cr(VI): N-p-chlorophenylbutyro H.A complexes,

| Solution | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| Vol. of (0.01) Cr (VI) in cm ³ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Vol. of pH 1 in cm ³ | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Vol. of dist. water cm ³ | 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 |
| Vol. of (0.01) H.A in cm ³ | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 |
| Vol. of chloroform added to H.A before added to M ^{tn} | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
| Mole fraction M/M+L | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
| Absorbance | 0.041 | 0.055 | 0.068 | 0.058 | 0.050 | 0.040 | 0.032 | 0.022 |

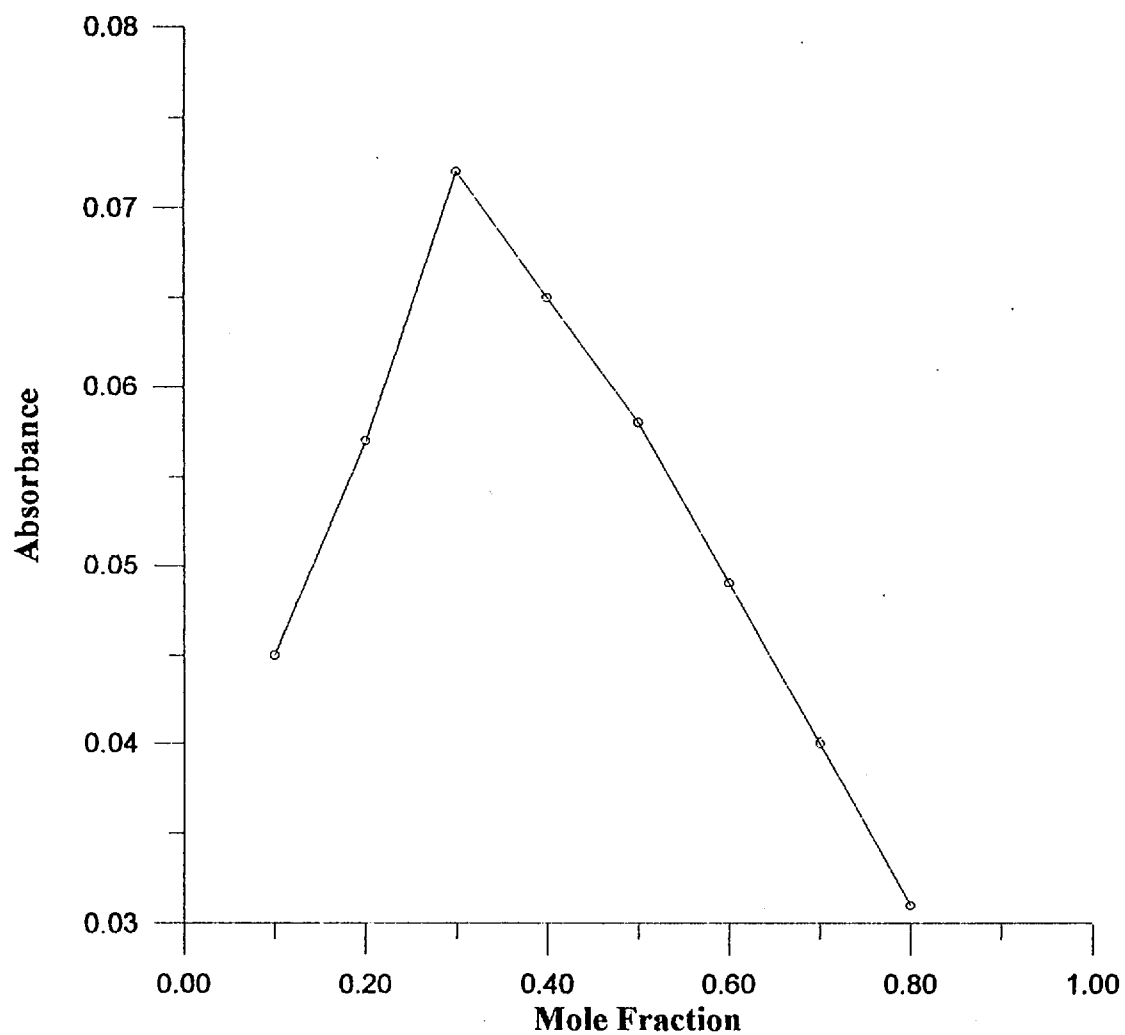


Fig. (4): Continuous Variation Curve Of N-phenylbutyrohydroxamic Acid- Cr (VI) Complex

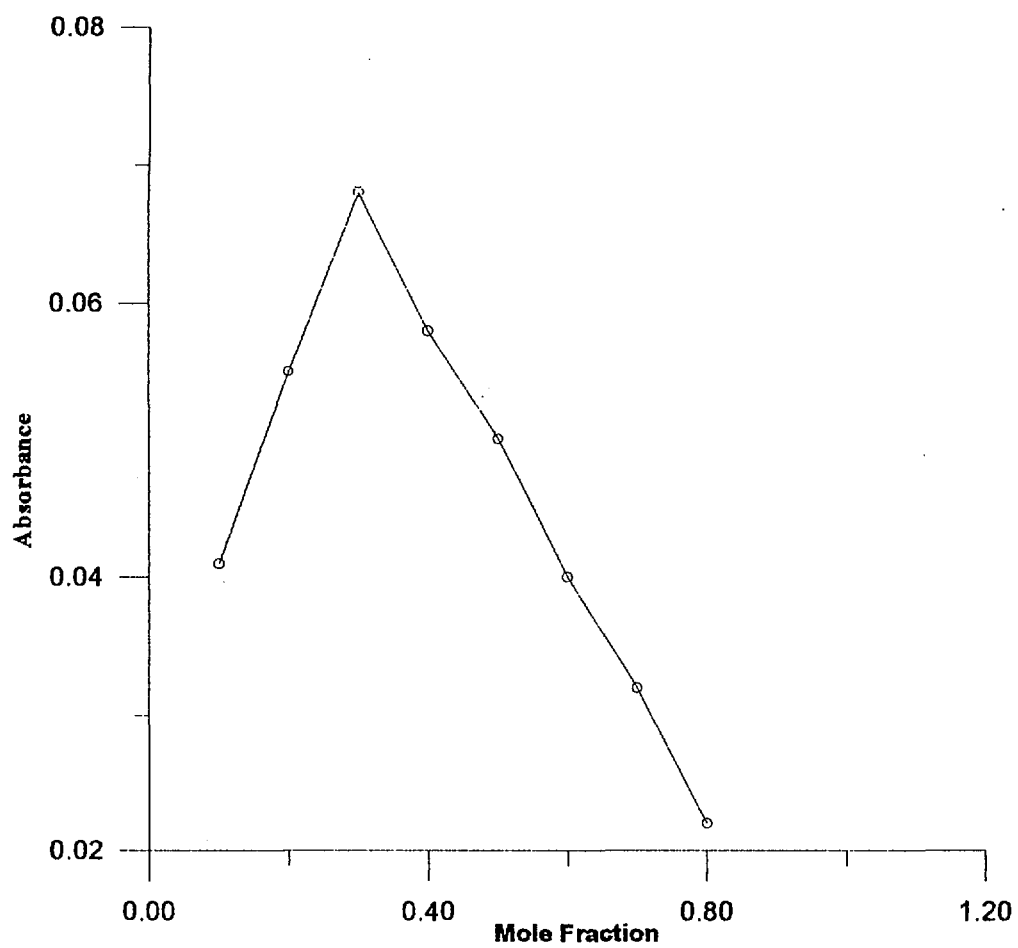


Fig. (5): Continuous Variation Curve Of p-Cl-phenylbutyroxamic Acid - Cr (VI) Complex

2.4.8- Suitability of The Two Acids For Spectrophotometric Determination of Cr (VI):

A series of concentration of Cr (VI) solution were extracted with the two hydroxamic acids at max. pH of extraction, the absorbance of yellow organic layers were measured against chloroform blank at 540 nm the readings were recorded in Table (6) using N-phenylbutyrohydroxamic acid and in Table (7) using N-p-Cl-phenylbutyrohydroxamic acid.

Table (6): Readings of N-phenylbutyro, H.A. for spectrophotometric determination of Cr(VI),

| Conc. in ppm | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|--------------|-------|-------|-------|-------|-------|
| Absorbance | 0.025 | 0.047 | 0.075 | 0.097 | 0.115 |

Table (7): Readings of N-p-chlorophenylbutyro, H.A for spectrophotometric determination of Cr(VI),

| Conc. in ppm | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|--------------|-------|-------|-------|-------|-------|
| Absorbance | 0.036 | 0.076 | 0.114 | 0.168 | 0.173 |

2.5- Extraction of Molybdenum (VI):

2.5.1- Preparation of Molybdenum (VI) Stock Solution:

1000 ppm of Mo (VI) was prepared by dissolving 1.8038 g of ammonium molybdate tetrahydrate $(\text{NH}_4)_6(\text{Mo}_7\text{O}_{24}) \cdot 4\text{H}_2\text{O}$ in distilled water. Transferred quantitatively to 1000cm³ volumetric flask and was completed to the mark with distilled water.

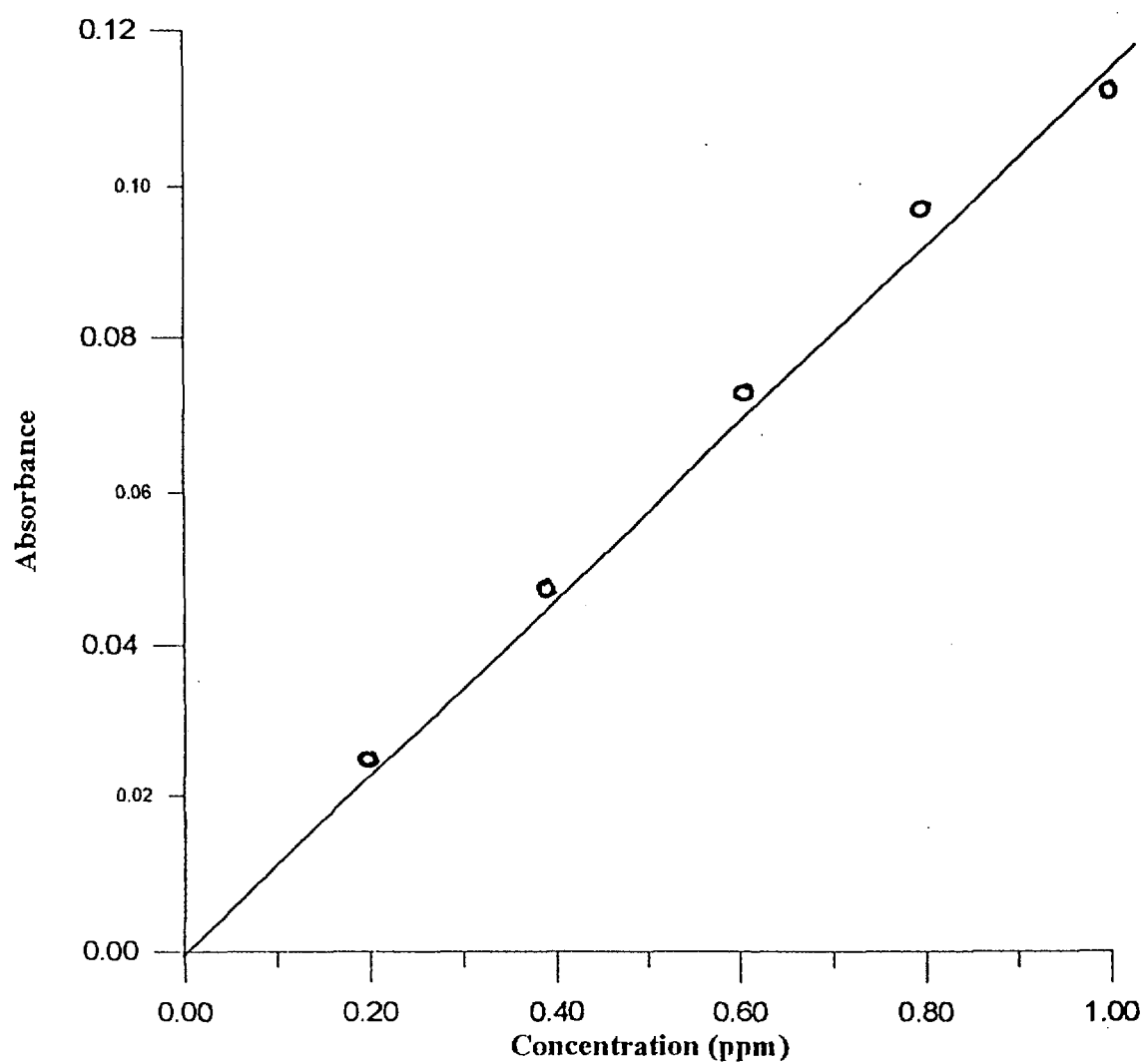


Fig. (6): Beer's Law Curve Of N-phenylbutyrohydroxamic Acid - Cr (VI) Complex

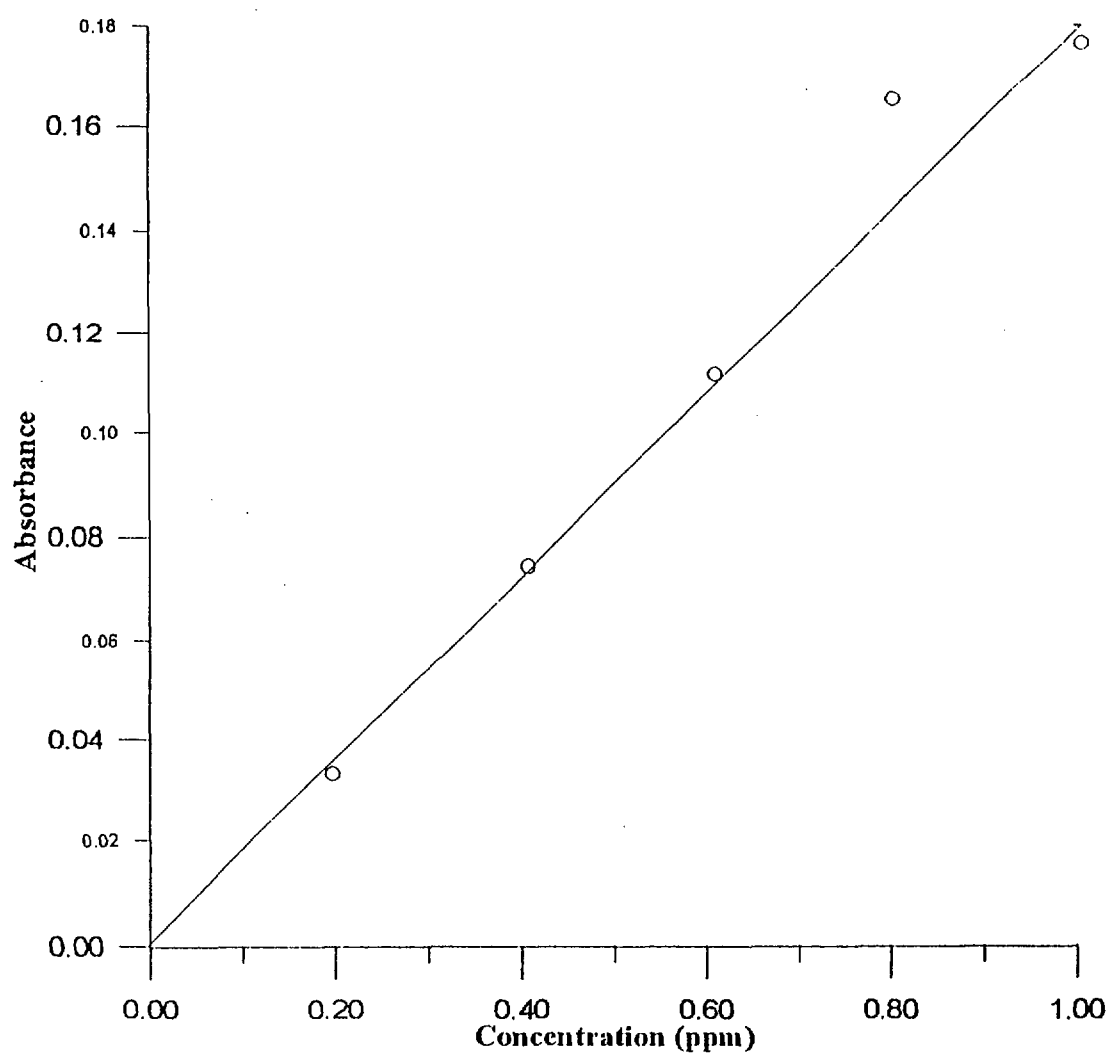


Fig. (7): Beer's Law Curve For N-p-Cl-phenylbutyrohydroxamic Acids - Cr (VI) Complex

Reagents:

- 1- 250 ppm Mo (VI) solution.
- 2- 50 ppm Mo (VI) solution.
- 3- 10% ferrous ammonium sulphate solution.
- 4- 10 % stannous chloride solution.
- 5- 10% potassium thiocyanate solution.
- 6- Di-isopropyl ether.
- 7- 0.02 M N-phenylbutyrylhydroxamic acid and 0.02 M N-p-Cl-phenylbutyrylhydroxamic acid.

2.5.2- Preparation of Standard Calibration Curve:

1, 2, 3, 4, 5 and 6 ppm of Mo (VI) solution were prepared by transferring 0.5, 1, 1.5, 2, 2.5 and 3 cm³ from 50 ppm Mo (VI) solution to six 25 cm³ volumetric flasks and completed to the mark with distilled water. The contents were transferred quantitatively to six, 100 cm³ separatory funnels, to each 2.0 cm³ of concentrated hydrochloric acid, 3.0 cm³ of ammonium ferrous sulphate and 3.0 cm³ of potassium thiocyanate solution were added. The solution was shaken gently and then 3.0 cm³ of 10 % stannous chloride solution was introduced.

The golden yellow solution was extracted twice with 10 cm³ di-isopropyl ether and finally with 5.0 cm³. The organic layers were collected in 25 cm³ volumetric flasks, the absorbance were measured at 465 nm in spectrophotometer against di-isopropyl ether blank, and the result were recorded in Table (8). The absorbance was plotted against concentration of Mo (VI) as shown in fig. (8).

2.5.3- Extraction of Mo (VI) With N-phenylbutyrohydroxamic Acid:

5.0 cm³ of 250 ppm Mo (VI) solution were transferred by a pipette to six 25 cm³ volumetric flasks and completed to mark with buffers from 1-6 to make the solution of 50 ppm Mo (VI) in each. The contents were transferred quantitatively to six, 100 cm³ separatory funnels, 25 cm³ of 0.02 M N-phenylbutyrohydroxamic acid were added and the separatory funnels were shaken gently for two minutes, the aqueous and organic layers were separated into different containers and the aqueous layers were kept for further analysis.

2.5.4- Determination of Mo (VI) In The Aqueous layer by The Thiocyanate

Method:

2.0 cm³ of an aliquots from each aqueous layer separated in (2.5.3), were transferred to six, 100 cm³ separatory funnels, to each 2.0 cm³ of conc. HCl, 3.0 cm³ of ammonium ferrous sulphate and 3.0 cm³ of potassium thiocyanate solution were added, the solution was shaken gently and then 3.0 cm³ stannous chloride solution was introduced, water was added to make the total value in each separatory funnel to 25 cm³. The golden yellow solution was extracted twice with 10 cm³ di-isopropyl ether and finally with 5 cm³, the organic layers were collected in 25 cm³ volumetric flask, the absorbance was read at 465 nm using 1.0 cm cell and the results were recorded in Table (9) the amount of Mo (VI) in the extracted aqueous layers was collected from calibration curve.

2.5.5- Extraction of Mo (VI) With p- chloro-phenylbutyrohydroxamic Acid:

The same procedures followed in (2.5.3) were applied except that N-p-Chlorophenylbutyrohydroxamic acid was used instead of N-phenylbutyrohydroxamic acid.

2.5.6- Determination of Mo (VI) In The Aqueous Layer By Thiocynate Method:

The procedure was as that followed in (2.5.4), the results were recorded in Table (10).

Table (8): standard calibration readings for Mo (VI)

| Conc. in ppm | 1 | 2 | 3 | 4 | 5 | 6 |
|--------------|-------|-------|-------|-------|-------|-------|
| Absorbance | 0.143 | 0.289 | 0.432 | 0.570 | 0.725 | 0.858 |

Table (9): Results of Extraction of Mo (VI) With N-p-phenylbutyrohydroxamic Acid:

| pH | Absorbance | % Remain | % Extracted |
|----|------------|----------|-------------|
| 1 | 0.035 | 06.25 | 93.75 |
| 2 | 0.075 | 12.50 | 87.50 |
| 3 | 0.139 | 23.75 | 76.25 |
| 4 | 0.191 | 32.50 | 67.50 |
| 5 | 0.230 | 40.00 | 60.00 |
| 6 | 0.302 | 52.50 | 47.50 |

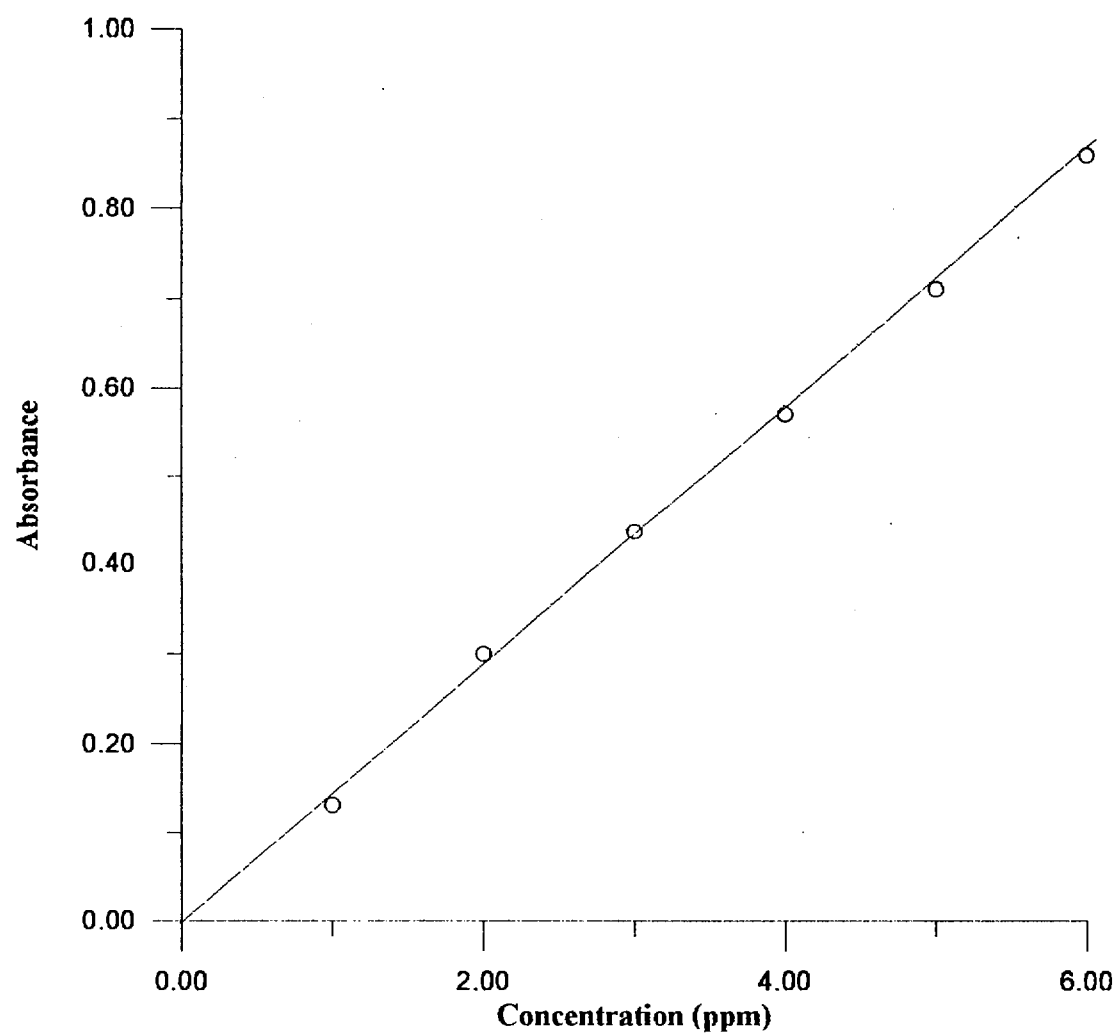


Fig. (8): Standard Calibration Curve For Mo (VI) With Thiocyanate

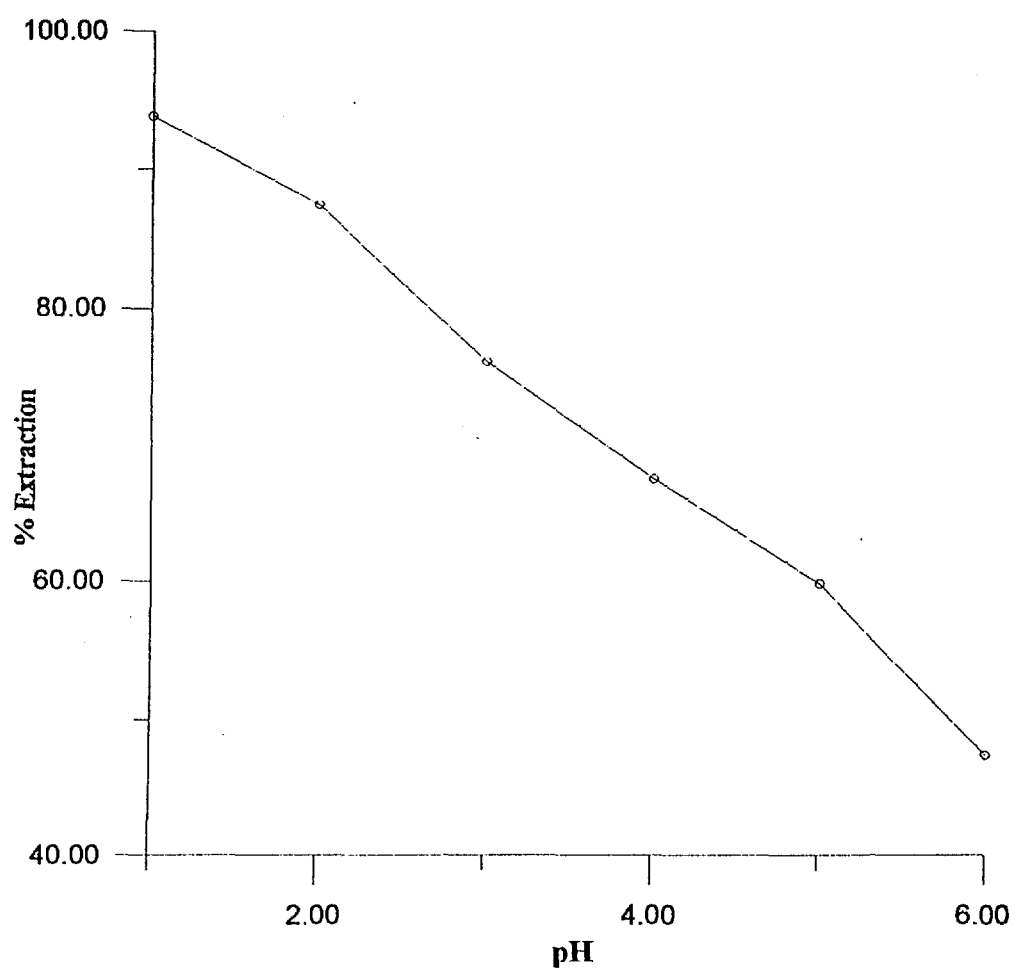


Fig. (9): % Of Extraction Of Mo (VI) with N-phenylbutyrohydroxamic Acid

Table (10): Results of Extraction of Mo (VI) With N-p-Chloro-phenylbutyrohydroxamic Acid:

| pH | Absorbance | % Remain | % Extracted |
|----|------------|----------|-------------|
| 1 | 0.150 | 26.25 | 73.75 |
| 2 | 0.192 | 32.50 | 67.50 |
| 3 | 0.250 | 43.75 | 56.25 |
| 4 | 0.330 | 56.25 | 43.75 |
| 5 | 0.416 | 70.00 | 30.00 |
| 6 | 0.537 | 93.70 | 06.30 |

2-6 Extraction of Titanium(IV):

2-6-1 Preparation of Titanium(IV) Stock Solution:

Standard Ti(IV) solution 1000 ppm was prepared by weighing 1.6680g of TiO_2 in platinum crucible, fused with 2g of potassium hydrogen sulphate and then dissolved in 5% H_2SO_4 , the volume was completed to 1000 cm^3 (neutralization of excess acid was carried out before using Ti (IV) for extraction).

Reagents:

- 1-Hydrogen peroxide 6%.
- 2-100 ppm Ti (IV) solution.
- 3- 4 M H_2SO_4 solution.
- 4- Buffers solution of pH 1-6.
- 5- 0.02M of N-phenylbutyrohydroxamic acid and p-chloro-phenylbutyrohydroxamic solution in chloroform .

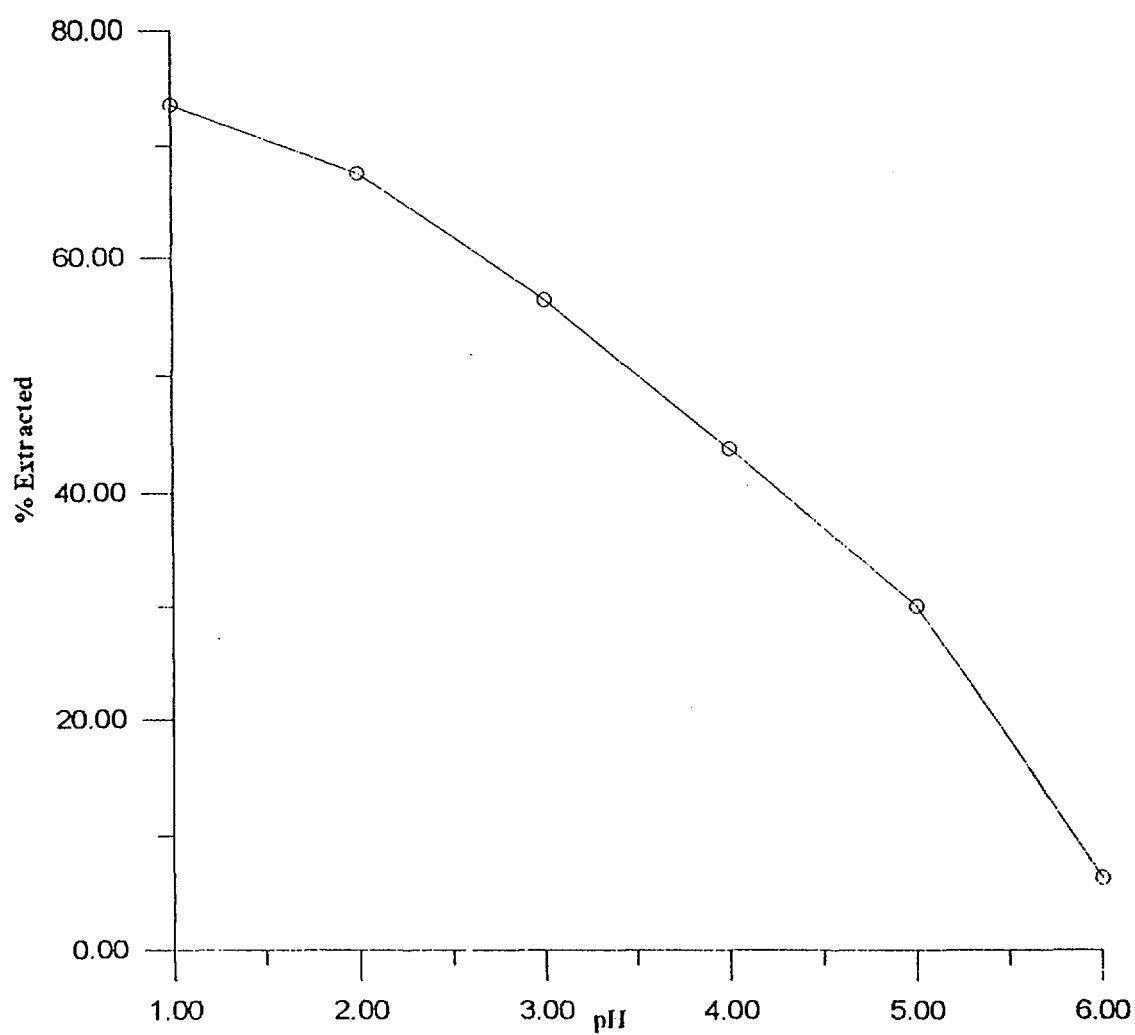


Fig (10): % Extraction Of Mo (VI) With N-p-Cl-phenylbutyroxamic Acid

2.6.2- Preparation of Standard Calibration Curve of Ti (IV):

Calibration curve was prepared by transferring 2.5, 5, 7.5, 10 and 12.5 cm³ of 100 ppm Ti (IV) solution in 25 cm³ volumetric flasks, 7.5 cm³ of 4 M H₂SO₄ were added to each flask in order to make the final acidity of the solution 1.2 M. Then 3 cm³ of 6% hydrogen peroxide were added to each flask a yellow colour formed, the final was completed 25 cm³ with distilled water, the absorbance was read at 410 nm using 1.0 cm cell, the results were recorded in Table (11), the absorbance was plotted against concentration of Ti (IV) as shown in fig. (11).

2.6.3- Extraction of Ti (IV) With N-phenylbutyrohydroxamic Acid:

5.0 cm³ portions from 600 ppm Ti (IV) solution were pipetted into a series of six 100 cm³ separatory funnels, 5.0 cm³ of buffers solution of pH 1 to 6 were added to each funnel. Then 10 cm³ of 0.02 M N-phenylbutyrohydroxamic acid were finally added. The contents were shaken gently for two minutes, the two layers were allowed to separate, and the aqueous layers were kept for further analysis.

2.6.4- Determination of Titanium (IV) In The Aqueous Layers:

1 cm³ from each aqueous layer separated in (2.6.3) was taken into 25 cm³ volumetric flask, then 7.5 cm³ of 4 M H₂SO₄ and 5.0 cm³ of 6% hydrogen peroxide were added, a yellow colour formed, and the volume was completed to 25 cm³ with distilled water. The absorbance of was read at 410 nm using 1 cm cell. The results results were recorded in Table (12). The amount of titanium was calculated from calibration curve.

2.6.5- Extraction of Ti(IV) With N-p-chloro-phenylbutyrohydroxamic Acid:

The same procedure followed in (2.6.3) were applied except that N-p-chloro-phenylbutyrohydroxamic acid was used instead of N-phenylbutyrohydroxamic acid.

2.2.6- Determination of Ti (IV) In Aqueous Layers:

The procedure was as that followed in (2.6.4). The absorbance was read at 410 nm using 1 cm cell and results were recorded in Table (13).

Table (11): Standard Calibration Readings For Ti (IV):

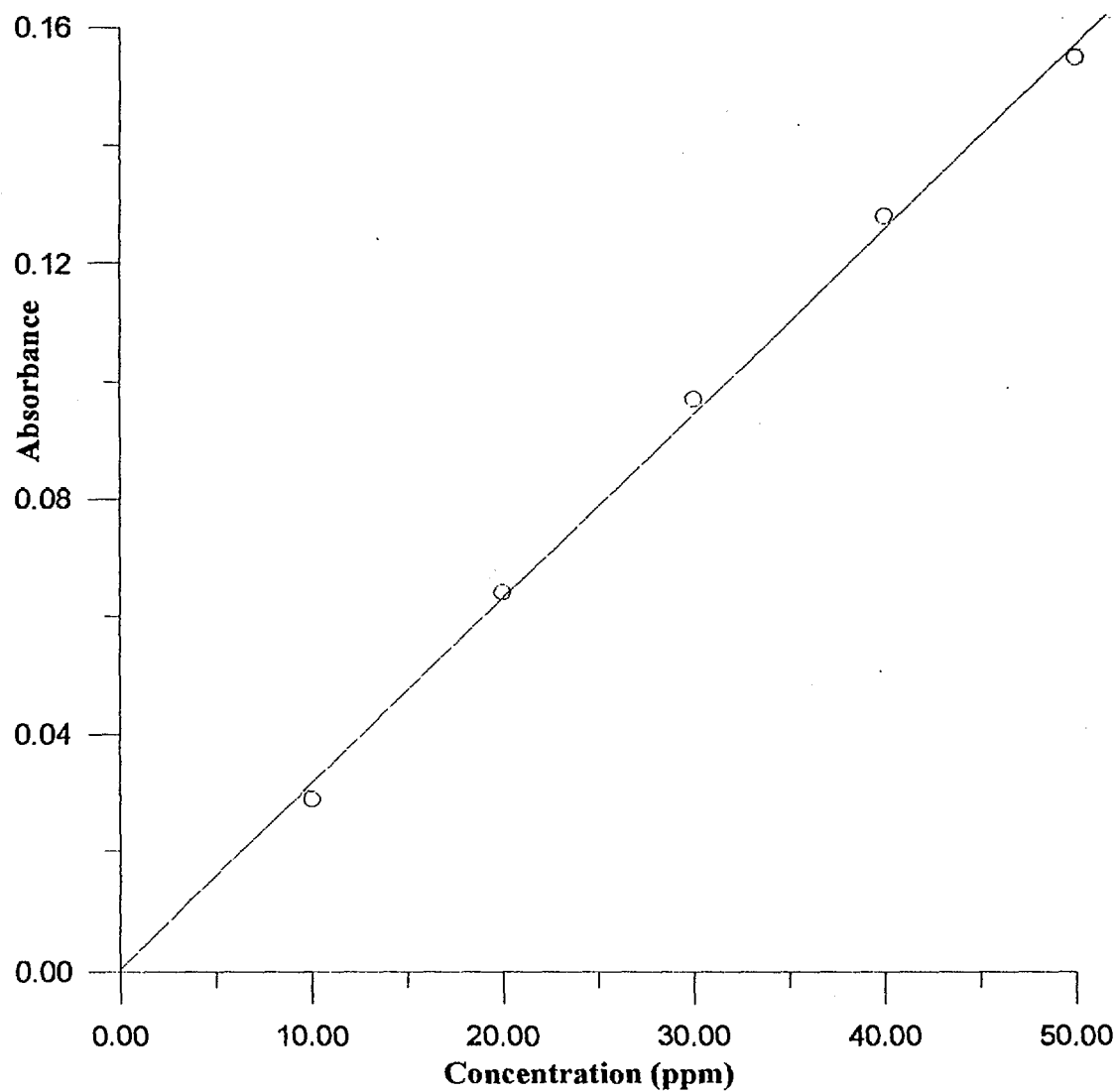
| Conc. ppm | 10 | 20 | 30 | 40 | 50 |
|------------|-------|-------|-------|--------|--------|
| Absorbance | 0.029 | 0.064 | 0.097 | 0.0128 | 0.0155 |

Table (12): Results Of Extraction Of Ti (IV) With N-phenylbutyrohydroxamic Acid:

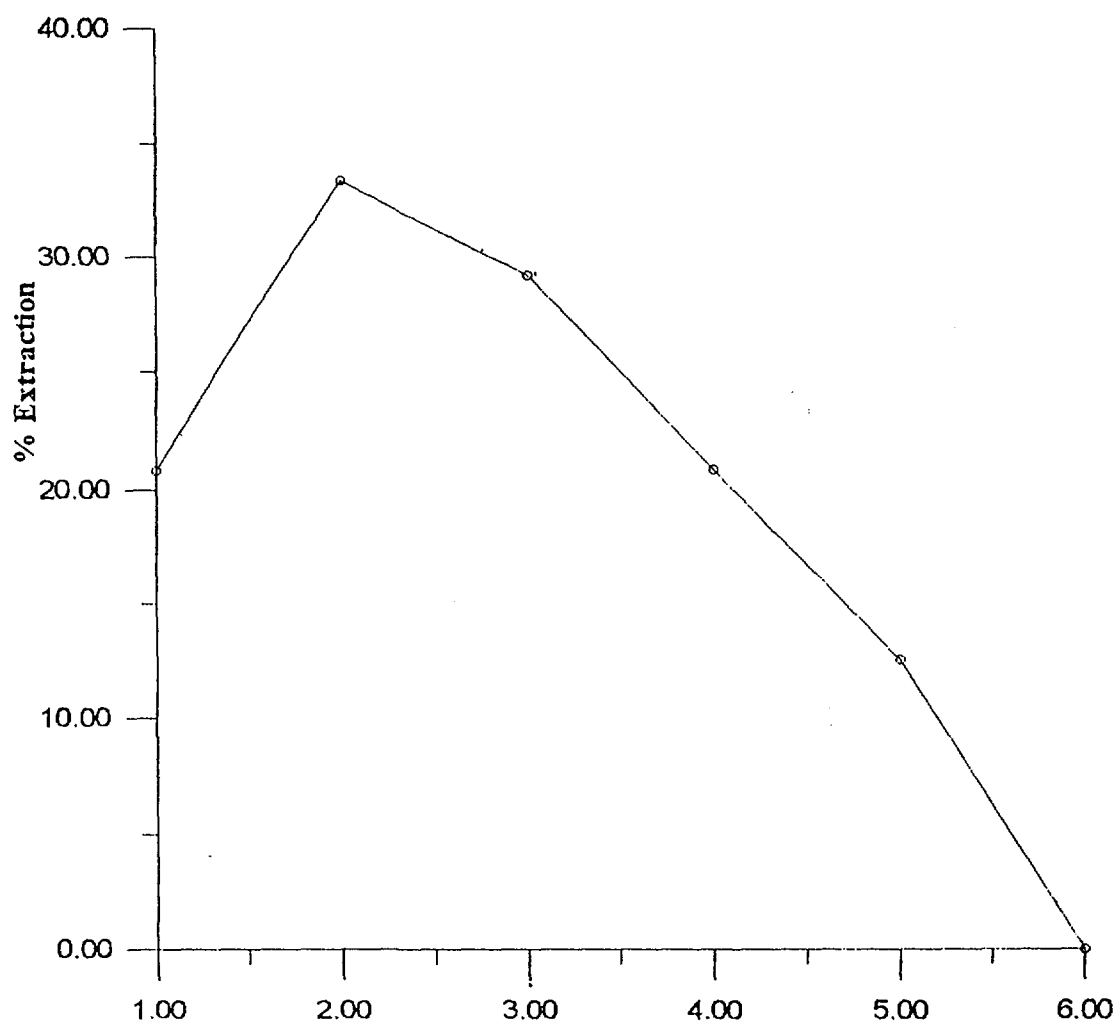
| pH | Absorbance | % Remain | % Extracted |
|----|------------|----------|-------------|
| 1 | 0.028 | 79.16 | 20.84 |
| 2 | 0.023 | 66.66 | 33.34 |
| 3 | 0.025 | 70.83 | 29.17 |
| 4 | 0.029 | 79.16 | 20.84 |
| 5 | 0.031 | 87.50 | 12.50 |
| 6 | 0.038 | 100.00 | 00.00 |

Table (13): Results of Extraction of Ti (IV) With N-p-Cl-phenylbutyrohydroxamic Acid

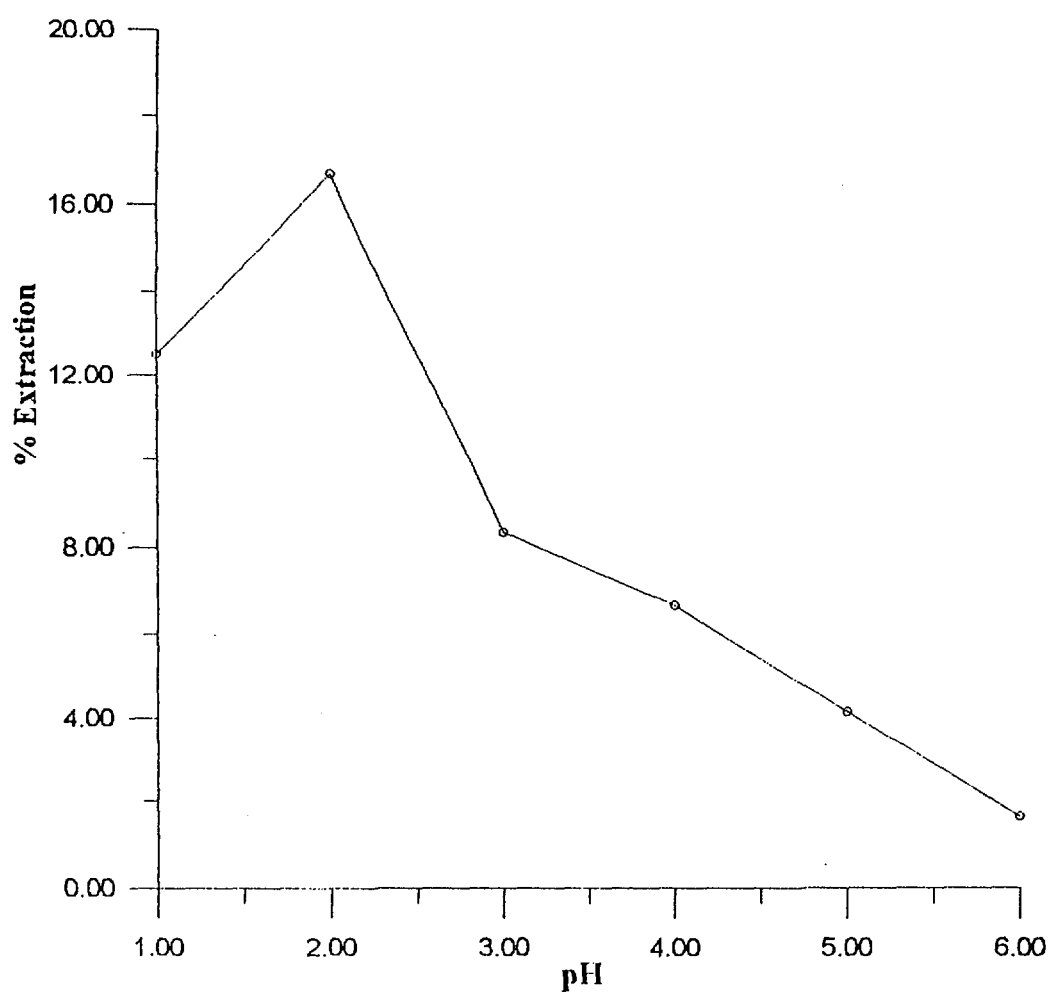
| pH | Absorbance | % Remain | % Extracted |
|----|------------|----------|-------------|
| 1 | 0.031 | 87.50 | 12.50 |
| 2 | 0.029 | 83.33 | 16.67 |
| 3 | 0.032 | 91.66 | 8.34 |
| 4 | 0.035 | 93.33 | 6.67 |
| 5 | 0.036 | 95.83 | 4.17 |
| 6 | 0.037 | 98.33 | 1.67 |



**Fig. (11): Standard Calibration Curve For Ti (IV)
With Hydrogen Peroxide**



**Fig.(12): % Of Extraction Of Ti (IV)
with N-phenylbutyhydroxamic Acid**



**Fig. (13): % Extraction Of Ti (IV)
With N-p-Cl-phenylbutyroxamic Acid**

2.6.7- Determination of The Ratio of Ti :HAs Complexes Using Continuous

Variation Method:

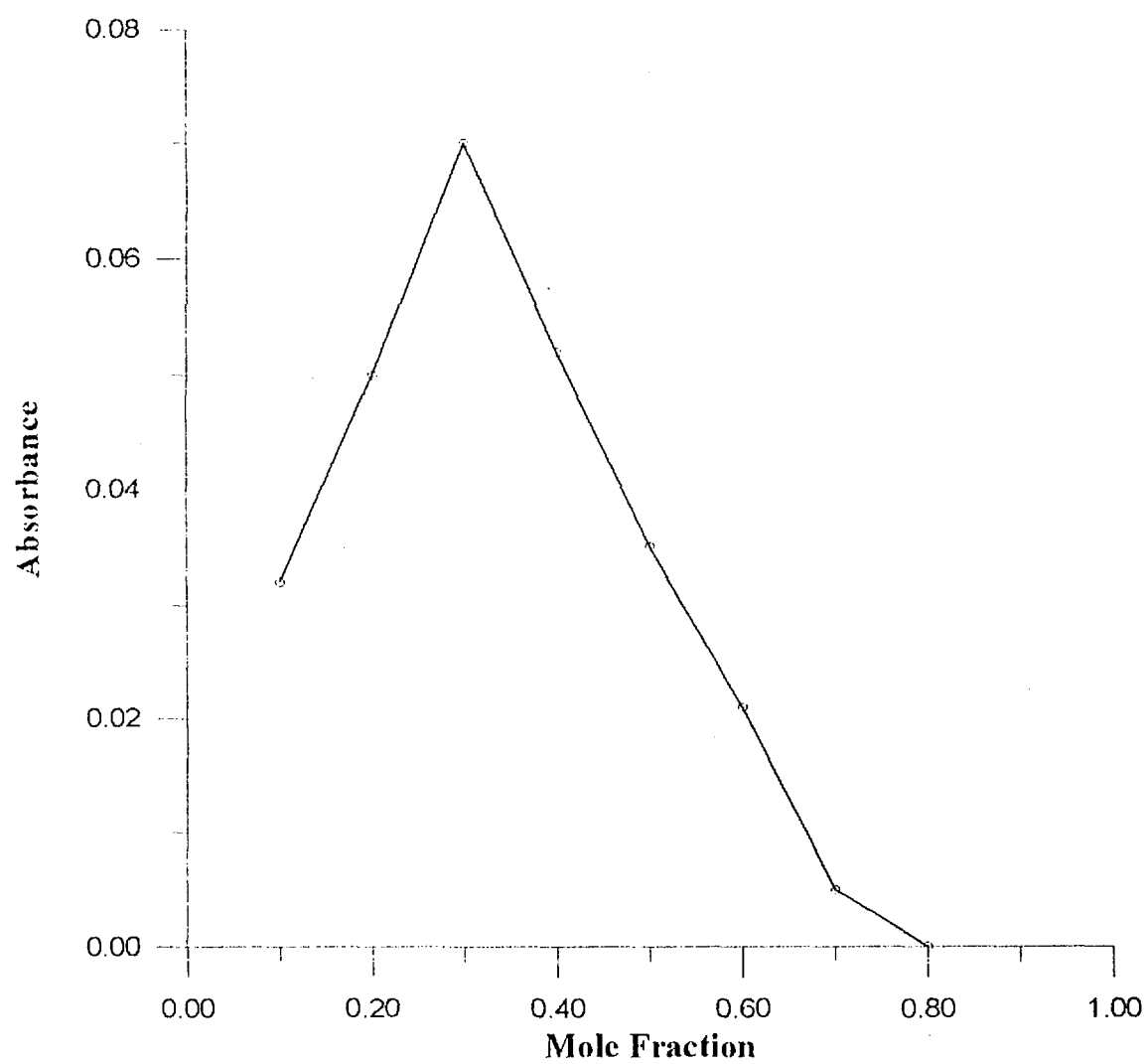
Series of extractions were carried out in which the mole fractions of Ti (IV) and two hydroxamic acids were varied from 0.2 to 0.8, the absorbance of organic layers was measured against the solvent chloroform as a blank at max. 410 nm. The results were recorded in Table (14) with N-phenylbutyrohydroxamic acid and Table (15) for N-p-Cl-phenylbutyrohydroxamic acid.

Table (14): Readings of the ratios of Ti(IV):
N-Phenylbutyro, H.A complexes,

| Solution | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| Vol. of (0.01) Ti (IV) in cm ³ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Vol. of pH 2 in cm ³ | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Vol. of dist. water in cm ³ | 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 |
| Vol. of (0.01) H.A in cm ³ | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 |
| Vol. Chloroform added to H.A before added to M ^{tn} | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
| mole fraction M/M+L | 0.01 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
| Absorbance | 0.048 | 0.065 | 0.086 | 0.072 | 0.061 | 0.050 | 0.036 | 0.003 |

Table (15): Readings of the ratios of Ti(IV): N-p-chlorophenylbutyrQH.A complexes,

| Solution | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|--|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| Vol. of (0.01) Ti (IV) in cm ³ | 1 10 | 2 10 | 3 10 | 4 10 | 5 10 | 6 10 | 7 10 | 8 10 |
| Vol. Of pH 2 in cm ³ | 14 | 13 | 12 | 11 | 10 | 9 | 8 | 7 |
| Vol. of dist. water in cm ³ | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 |
| Vol. of (0.01) H.A in cm ³ | | | | | | | | |
| Vol. Chloroform added to H.A before added to M ⁴⁺ | 16 0.01 | 17 0.2 | 18 0.3 | 19 0.4 | 20 0.5 | 21 0.6 | 22 0.7 | 23 0.8 |
| mole fraction M/M+L | 0.032 | 0.050 | 0.070 | 0.052 | 0.035 | 0.021 | 0.005 | 0.0 |
| Absorbance | | | | | | | | |



**Fig. (14): Continuous Variation Curve Of
N-phenylbutyrohydroxamic Acid Ti (IV) Complex**

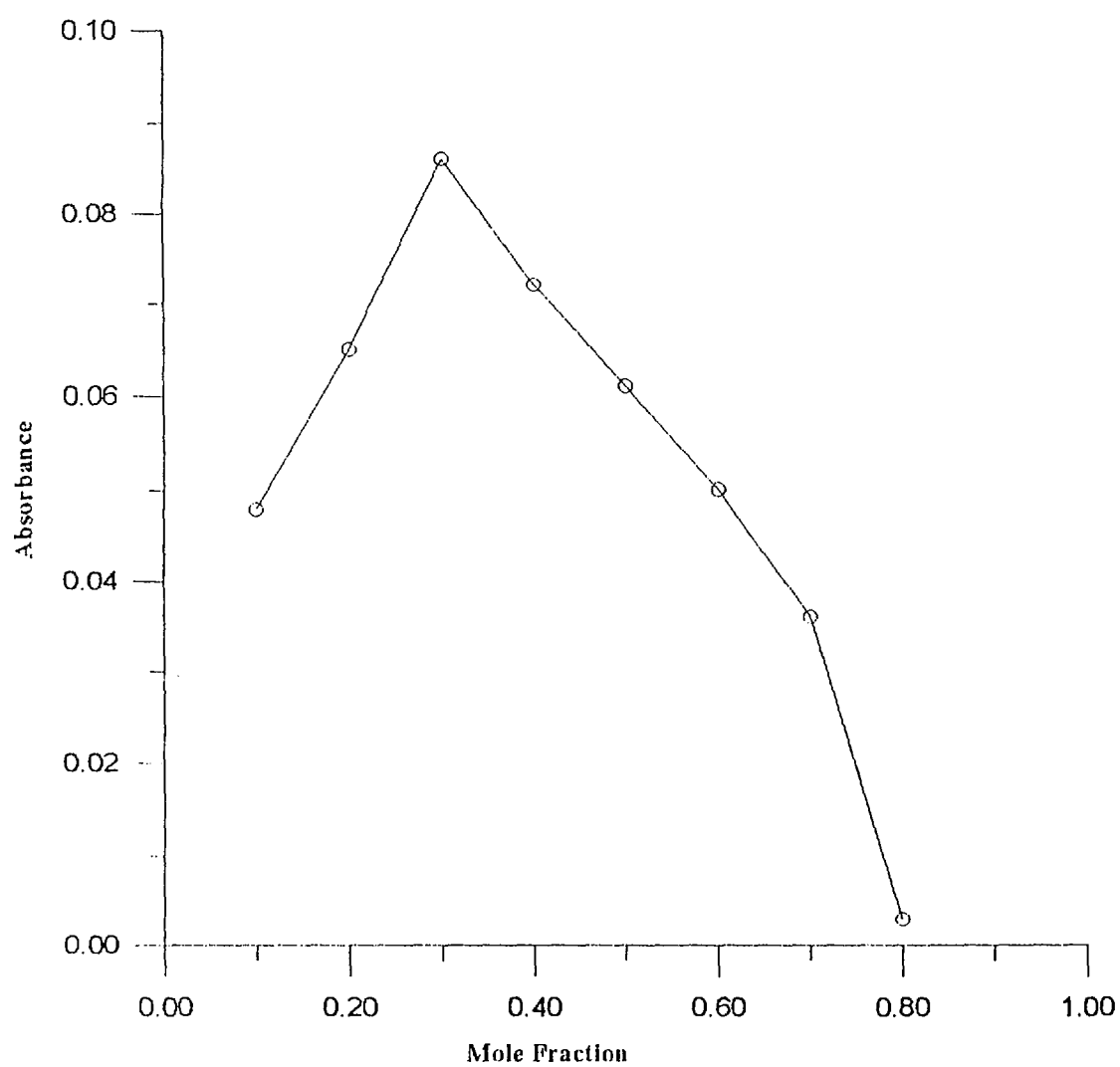


Fig. (15): Continuous Variation Curve Of N-p-Cl-phenylbutyroxamic Acid-Ti (IV) Complex

2.6.8- Suitability Of The Two Acids For Spectrophotometric Determination Of

Ti (IV):

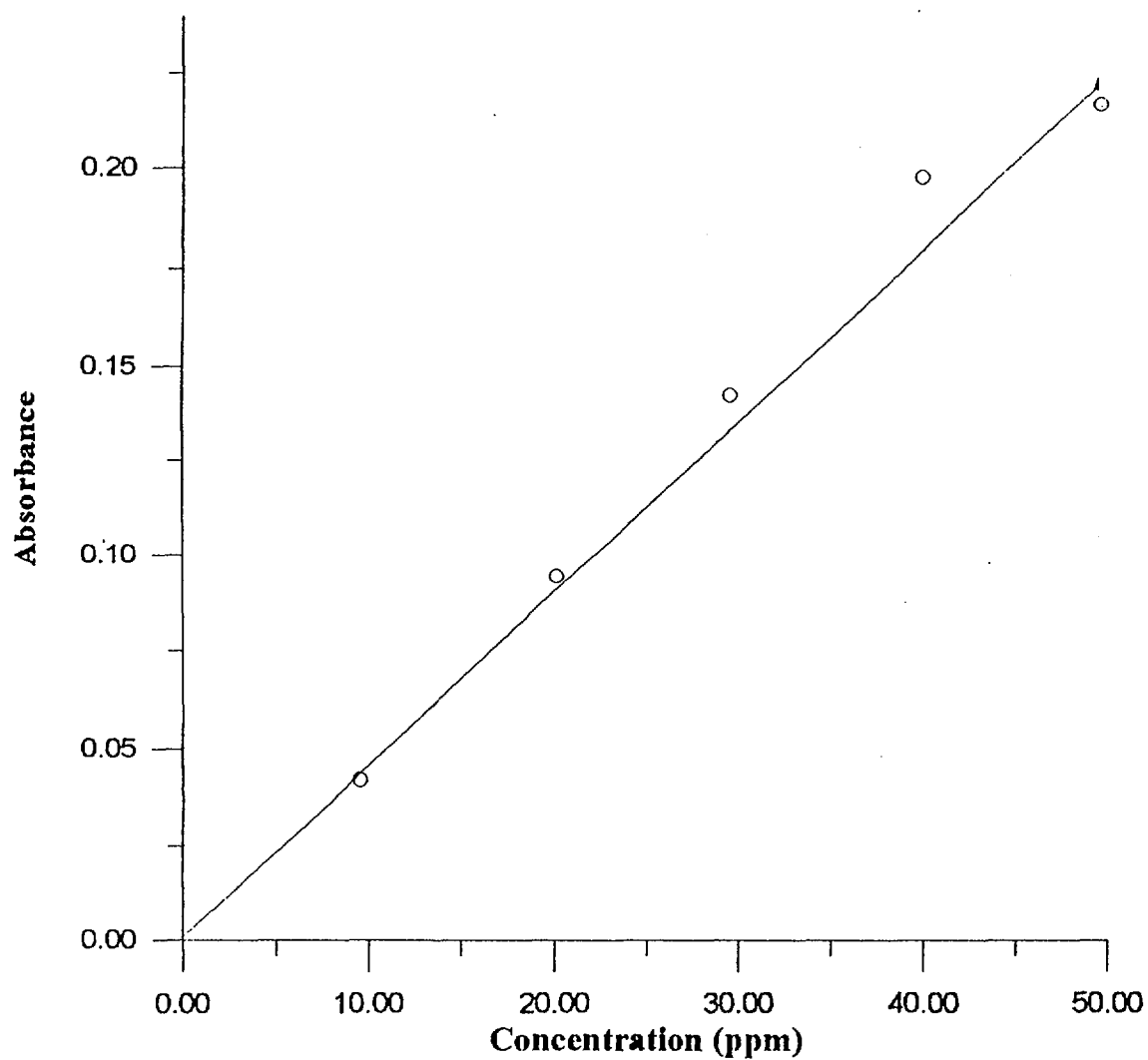
Series of concentrations of Ti (IV) solution were extracted with two hydroxamic acids at max. of pH extraction. The absorbance of the yellow extracts were measured against chloroform blank at 410 nm. The readings were recorded in Table (16) using N-phenylbutyrohydroxamic acid and shown in figure (16) & Table (17) using N-p-Cl-phenylbutyrohydroxamic acid.

Table (16) Readings of N-phenylbutyroH.A for spectrophotometric determination of Ti(IV).

| Conc. ppm | 10 | 20 | 30 | 40 | 50 |
|------------|-------|-------|-------|-------|-------|
| Absorbance | 0.048 | 0.094 | 0.141 | 0.197 | 0.214 |

Table (17) Readings of N-p-chlorophenylbutyroH.A for spectrophotometric determination of Ti(IV).

| Conc. ppm | 10 | 20 | 30 | 40 | 50 |
|------------|-------|-------|-------|-------|-------|
| Absorbance | 0.035 | 0.074 | 0.099 | 0.143 | 0.165 |



**Fig. (16): Beer's Law Curve Of N-phenylburyrohydroxamic
Acid Ti (IV) Complex**

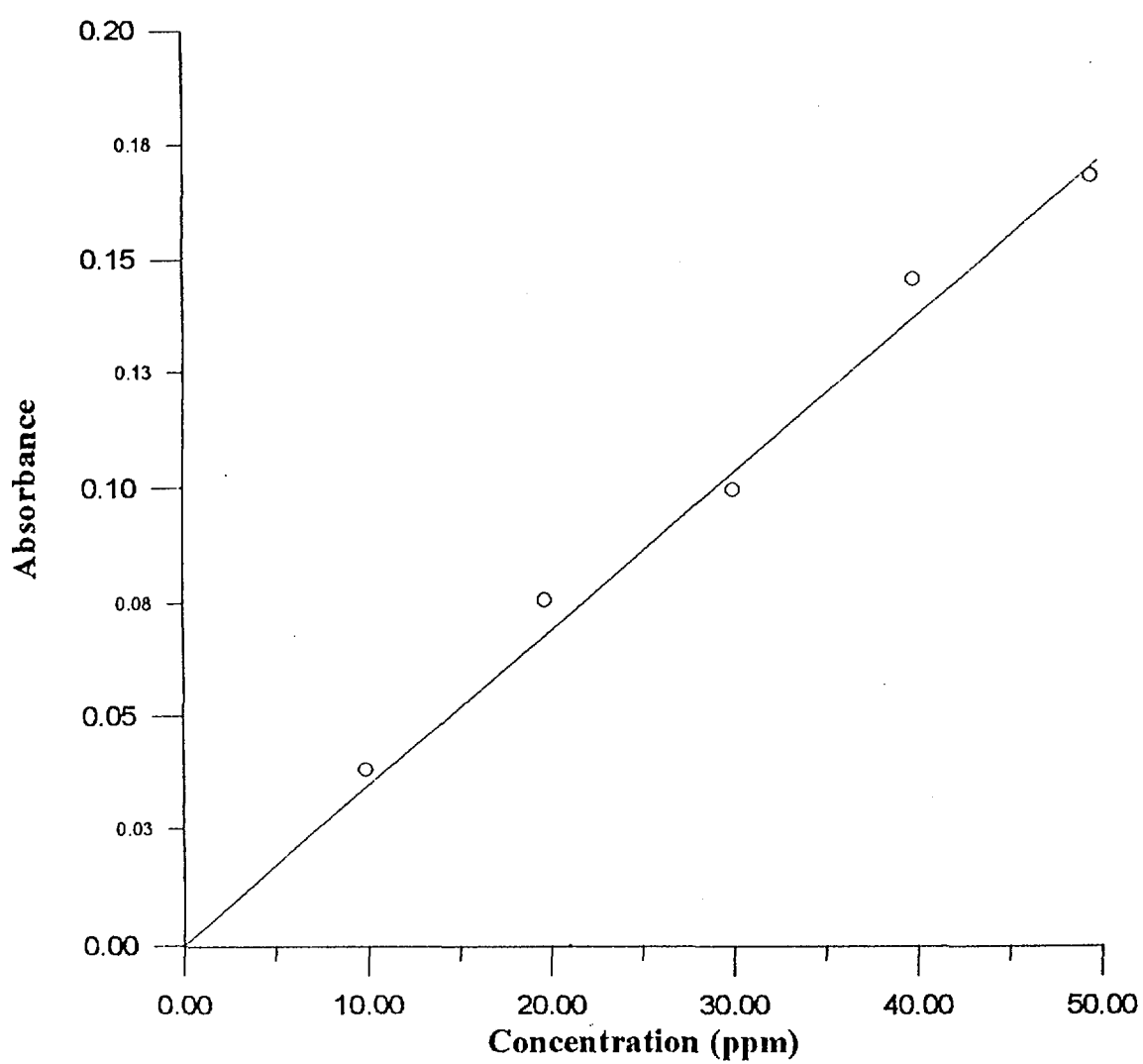


Fig. (17): Beer's Law Curve Of N-p-Chlorophenylbutyroydroxamic Acid Ti (IV) Complex

2.7- Extraction of Uranium (VI):

250 ppm U (VI) was prepared using by dissolving 0.2226g of uranyl acetate



In distilled water, transferred quantitatively to 500 cm³ volumetric flask and completed to the mark with distilled water.

Reagents:

- 1- 50 ppm and 250 ppm of U (VI) solution.
- 2- 1% (w/v) 8-hydroxyquinoline in chloroform.
- 3- 0.02 M aqueous solution of ethylenedi-amine tetra acetic acid (disodium salt).
- 4- Buffers solution from pH 1 to 10 & pH 8.8.
- 5- 0.02 M chloroform solution of N-phenylbutyro, and N-p-Cl-phenylbutyrohydroxamic acids.

2.7.2- Preparation of Standard Calibration Curve:

A calibration curve of U (VI) was constructed by placing 1, 2, 3, 4, and 5 cm³ of 50 ppm Uranium solution into a series of ten, 100 cm³ separatory funnels. 10 cm³ of 8.8 buffer and 5.0 cm³ of 0.02 M EDTA were added to each separatory funnel and the volume was completed to 25 cm³ with distilled water. The solutions were shaken gently for two minutes with 10, 10 and 5.0 cm³ of 1% (w/v) 8-hydroxyquinoline. The organic layers were collected in 25 cm³ volumetric flask and completed to the mark with chloroform. The absorbance of hydroxyquinoline - U (VI) complex of the standard solution were measured at 400 nm against chloroform blank and results were recorded in Table (18). The absorbance was plotted against concentration as shown in figure (18)

2.7.3- Extraction of U (VI) With N-phenylbutyrohydroxamic Acid:

5.0 cm³ of 250 ppm Uranium (VI) solution were pipetted into a series of ten, 100 cm³ separatory funnels, 5.0 cm³ of buffer solution of pH 1 to 10 and 10 cm³ of N-phenylbutyrohydroxamic acid were added the content were shaken gently for two minutes, then, the two layers were separated into different flasks, the aqueous layers were kept for further analysis.

2.7.4- Determination of U (VI) In The Aqueous Layer By 8-hydroxyquinoline:

From each aqueous layer separated in (2.7.3), 1.0 cm³ was pipetted into a series of ten, 100 cm³ separatory funnels. 10 cm³ of 8.8 buffer were introduced and 5.0 cm³ of 0.02 M EDTA solution was added the volume was completed to 25 cm³ with distilled water. The yellow solution was extract twice with 10 cm³ with 8-hydroxyquinoline and finally with 5.0 cm³. The organic extract were collected in 25 cm³ volumetric flask, the absorbance of the yellow layer was measured at 400 nm using 1 cell against chloroform blank and results were recorded in Table (19). The amount of Uranium (VI) extracted was calculated from calibration curve.

2.7.5- Extraction of U(VI) With N-p-chlorophenyl-butyrohydroxamic Acid:

The same procedures followed in (2.7.3) were applied except that N-p-Cl-phenylbutyrohydroxamic acid was used instead of N-phenylbutyrohydroxamic acid.

2.7.6- Determination of U (VI) In Aqueous Layer By The 8-hydroxyquinoline:

The procedure was as that followed in (2.7.4). The absorbance of the chloroform solution of the aqueous solution were read at 400 nm and results were recorded in Table (20).

Table (18): Standard Calibration Curve Readings For U(VI):

| Conc. ppm | 2 | 4 | 6 | 8 | 10 |
|------------|-------|-------|-------|-------|-------|
| Absorbance | 0.055 | 0.109 | 0.150 | 0.205 | 0.250 |

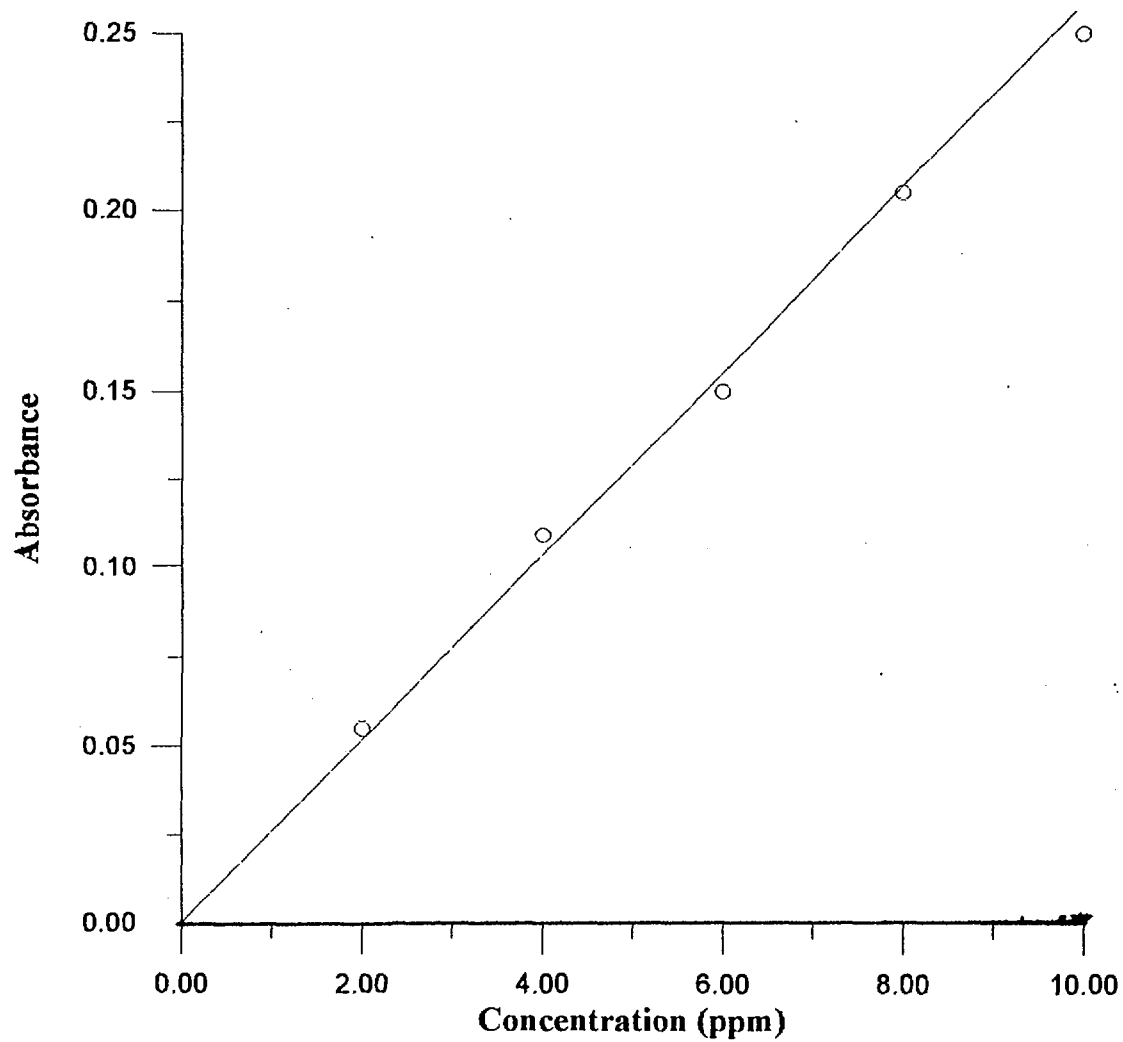
Table (19): Results of Extraction of U (VI) With N-phenylbutyrohydroxamic**Acid:**

| pH | Absorbance | % Remain | % Extracted |
|----|------------|----------|-------------|
| 1 | 0.131 | 100.00 | 0.00 |
| 2 | 0.131 | 100.00 | 0.00 |
| 3 | 0.130 | 100.00 | 0.00 |
| 4 | 0.110 | 84.00 | 16.00 |
| 5 | 0.078 | 58.00 | 42.00 |
| 6 | 0.040 | 28.00 | 72.00 |
| 7 | 0.050 | 36.00 | 64.00 |
| 8 | 0.063 | 48.00 | 52.00 |
| 9 | 0.098 | 74.00 | 26.00 |
| 10 | 0.108 | 82.00 | 18.00 |

Table (20): Results of Extraction of U (VI) With p-Cl-phenylbutyrohydroxamic

Acid:

| pH | Absorbance | % Remain | % Extracted |
|-----------|-------------------|-----------------|--------------------|
| 1 | 0.130 | 100.00 | 0.00 |
| 2 | 0.129 | 100.00 | 0.00 |
| 3 | 0.126 | 98.00 | 2.00 |
| 4 | 0.107 | 82.00 | 18.00 |
| 5 | 0.070 | 52.00 | 48.00 |
| 6 | 0.035 | 24.00 | 76.00 |
| 7 | 0.050 | 36.00 | 64.00 |
| 8 | 0.078 | 58.00 | 42.00 |
| 9 | 0.090 | 66.00 | 34.00 |
| 10 | 0.115 | 88.00 | 12.00 |



**Fig. (18): Standard Calibration Curve For U (VI)
With 8-hydroxyquinoline**

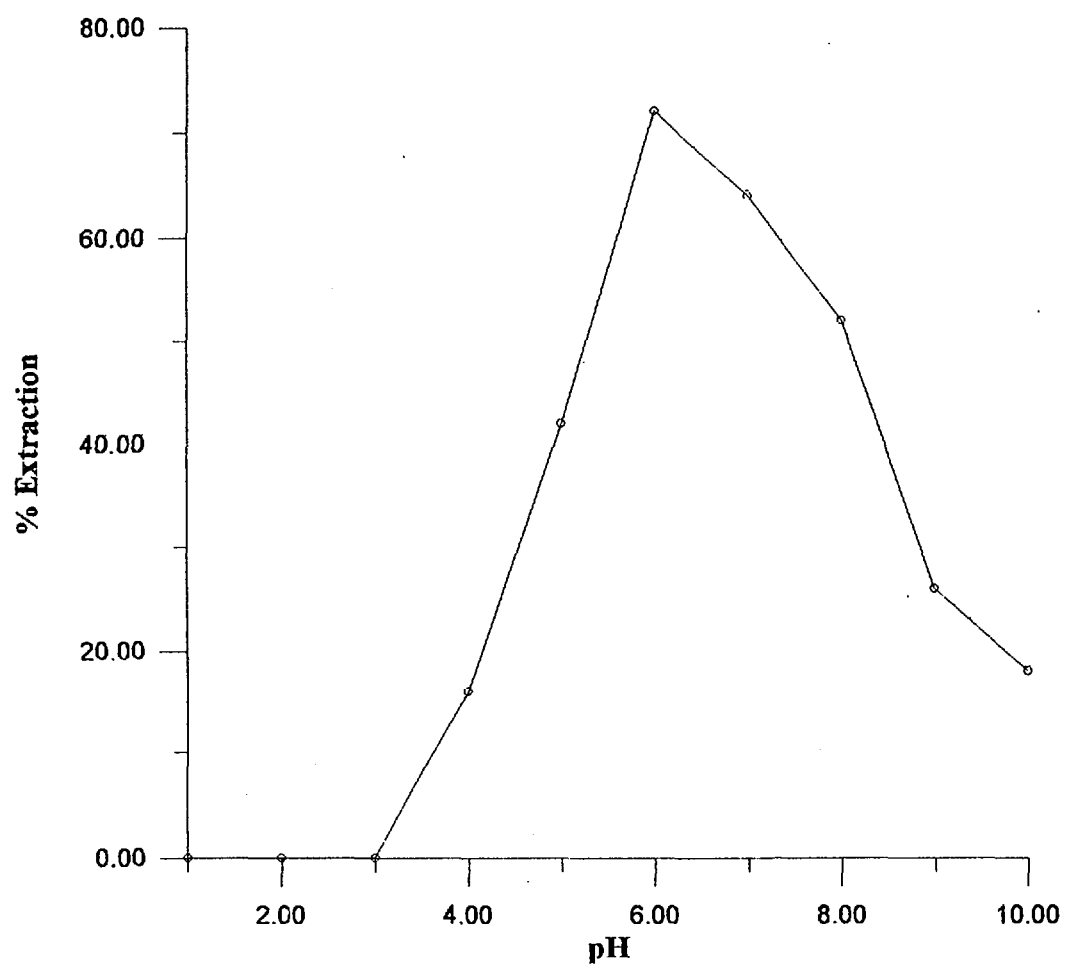
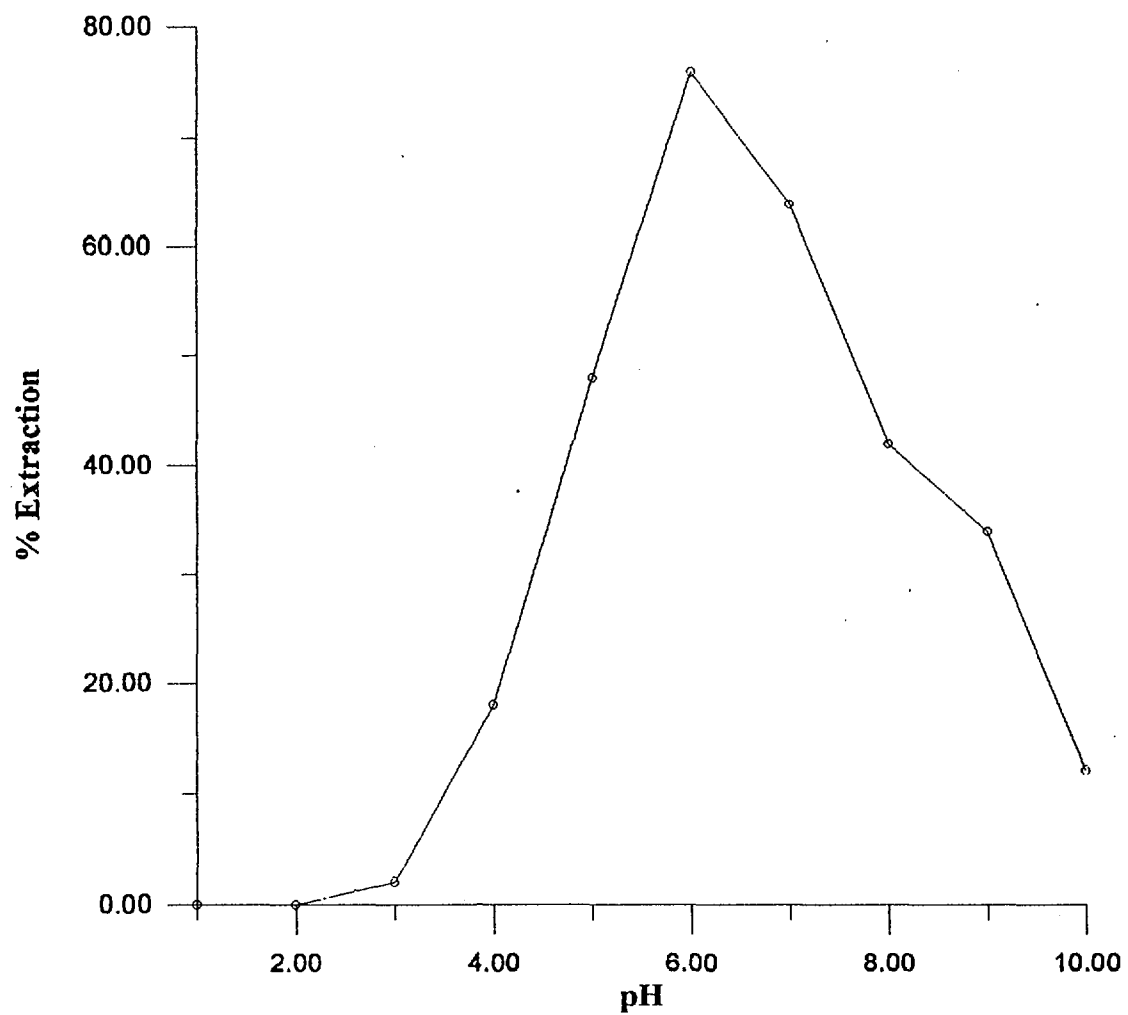


Fig. (19): % Extraction Of U (VI) With N-phenylbutyrylhydroxamic Acid



**Fig. (20): % Extraction Of U (VI)
With N-p-Cl-phenylbutyroxamic Acid**

2.7.7- Determination of The Ratio of U (VI):Hydroxamic Acid Complex, Using

Continuous Variation Method:

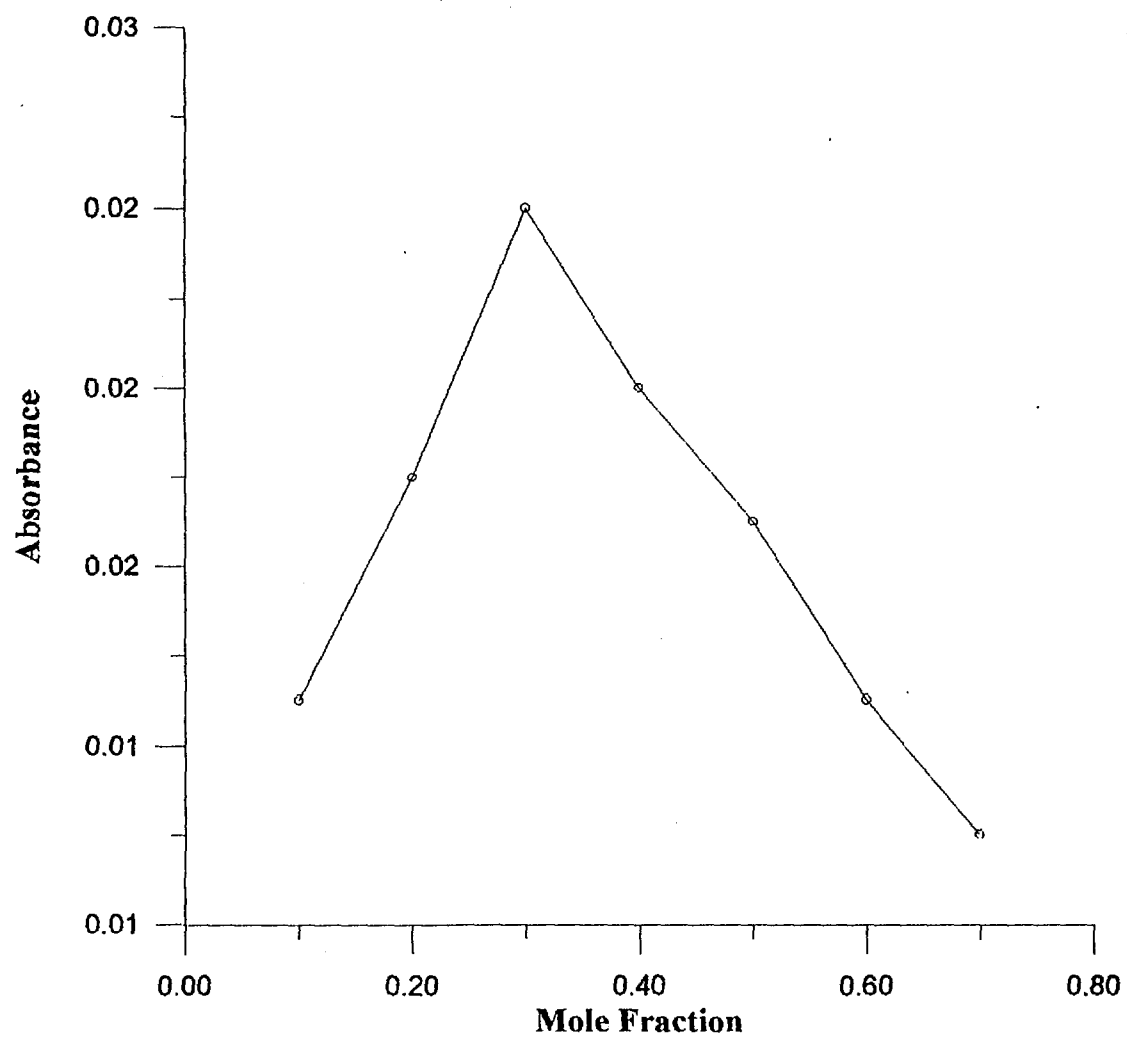
A series of extractions were carried out in which the mole fraction of U (VI) with N-phenylbutyrohydroxamic acid and with N-p-chloro-phenylbutyrohydroxamic acid were varied from 0.2 to 0.8 respectively. Absorbance of organic layers were measured against the solvent chloroform as a blank at 400 nm. Results are shown in Table (21) & (22). The absorbance was plotted against mole fraction as shown in figure (21) & (22).

Table (21): Readings of the ratios of U(VI):
N-Phenylbutyro, H.A complexes,

| Solution | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|-------|-------|-------|-------|-------|-------|-------|
| Vol. Of (0.01) U (VI) in cm ³ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Vol. Of pH 6 in cm ³ | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Vol. Of distilled water in cm ³ | 14 | 13 | 12 | 11 | 10 | 9 | 8 |
| Vol. Of (0.01) N-phenyl-butyro-hydroxamic acid in cm ³ | 9 | 8 | 7 | 6 | 5 | 4 | 3 |
| Vol. Of chloroform added to ligand before added to U (VI) | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| Mole fraction of U (VI) | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 |
| Absorbance | 0.013 | 0.018 | 0.024 | 0.020 | 0.017 | 0.013 | 0.010 |

**Readings of the ratios of U(VI): N-p-chloro
Table (22) phenylbutyro,H.A complexes,**

| Solution | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|--|-------|-------|-------|-------|-------|-------|-------|
| Vol. Of (0.01) U (VI) in cm ³ | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Vol. Of pH 6 in cm ³ | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Vol. Of distilled water in cm ³ | 14 | 13 | 12 | 11 | 10 | 9 | 8 |
| Vol. Of (0.01) N-p-Cl-phenyl- butyro-hydroxamic acid in cm ³ | 9 | 8 | 7 | 6 | 5 | 4 | 3 |
| Vol. Of chloroform added to ligand before added to U (VI) | 16 | 17 | 18 | 19 | 20 | 21 | 22 |
| Mole fraction of U (VI) | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 |
| Absorbance | 0.015 | 0.017 | 0.020 | 0.017 | 0.014 | 0.011 | 0.005 |



**Fig. (21): Continuous Variation Curve Of
N-phenylbutyrohydroxamic Acid- U (VI) Complex**

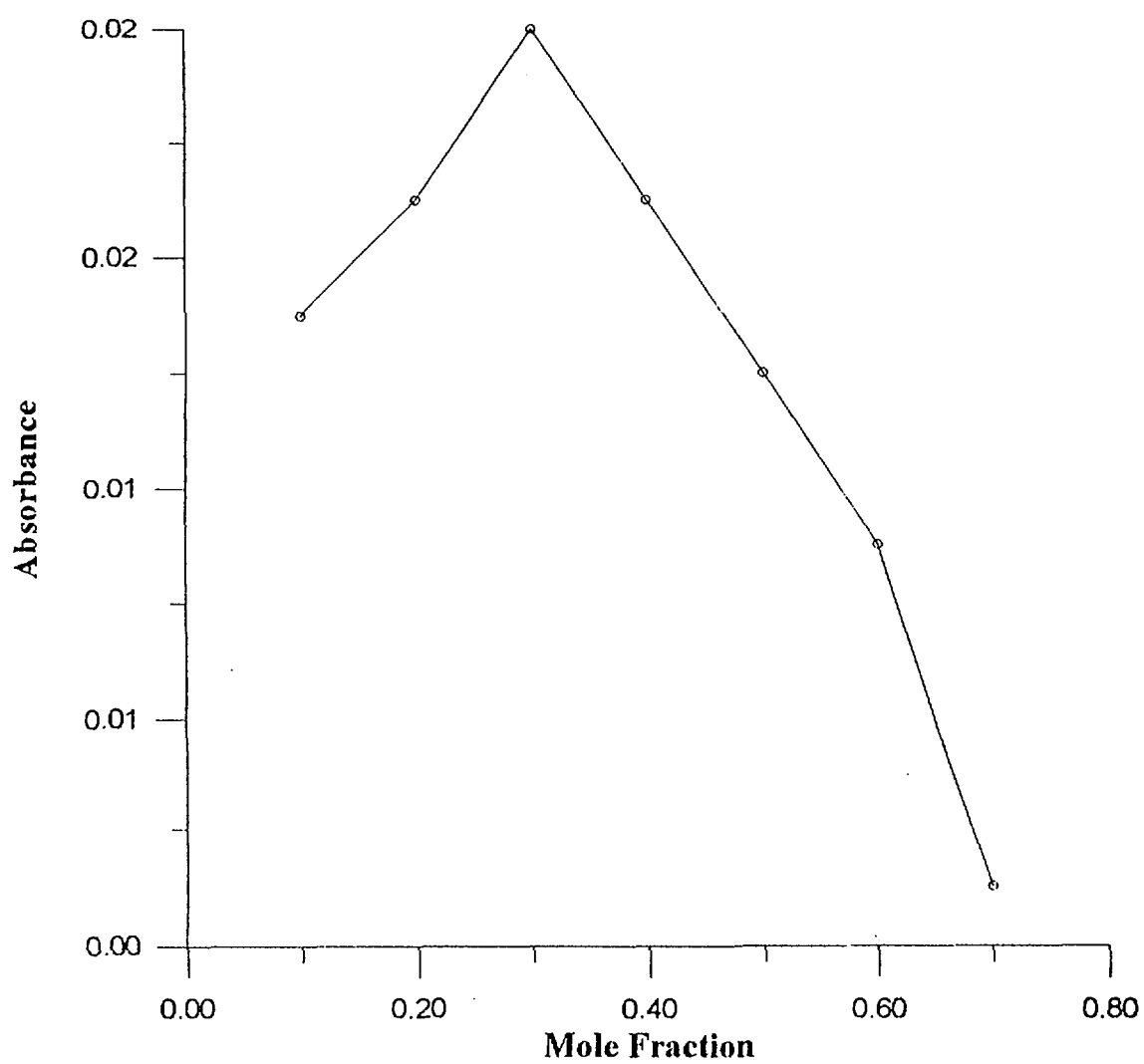


Fig. (22): Continuous Variation Curve Of N-p-Cl-phenylbutyroxamic Acid - U (VI) Complex

2.7.8- Suitability of The Two Acids For Spectrophotometric Determination of

U (VI):

The same procedure followed in (2.4.8) was applied using different concentration of U (VI) solution.

The readings were recorded in Table (23) using N-phenylbutyrohydroxamic acid.

Figure (23) and Table (24) using N-p-Cl-phenylbutyrohydroxamic acid, fig. (24).

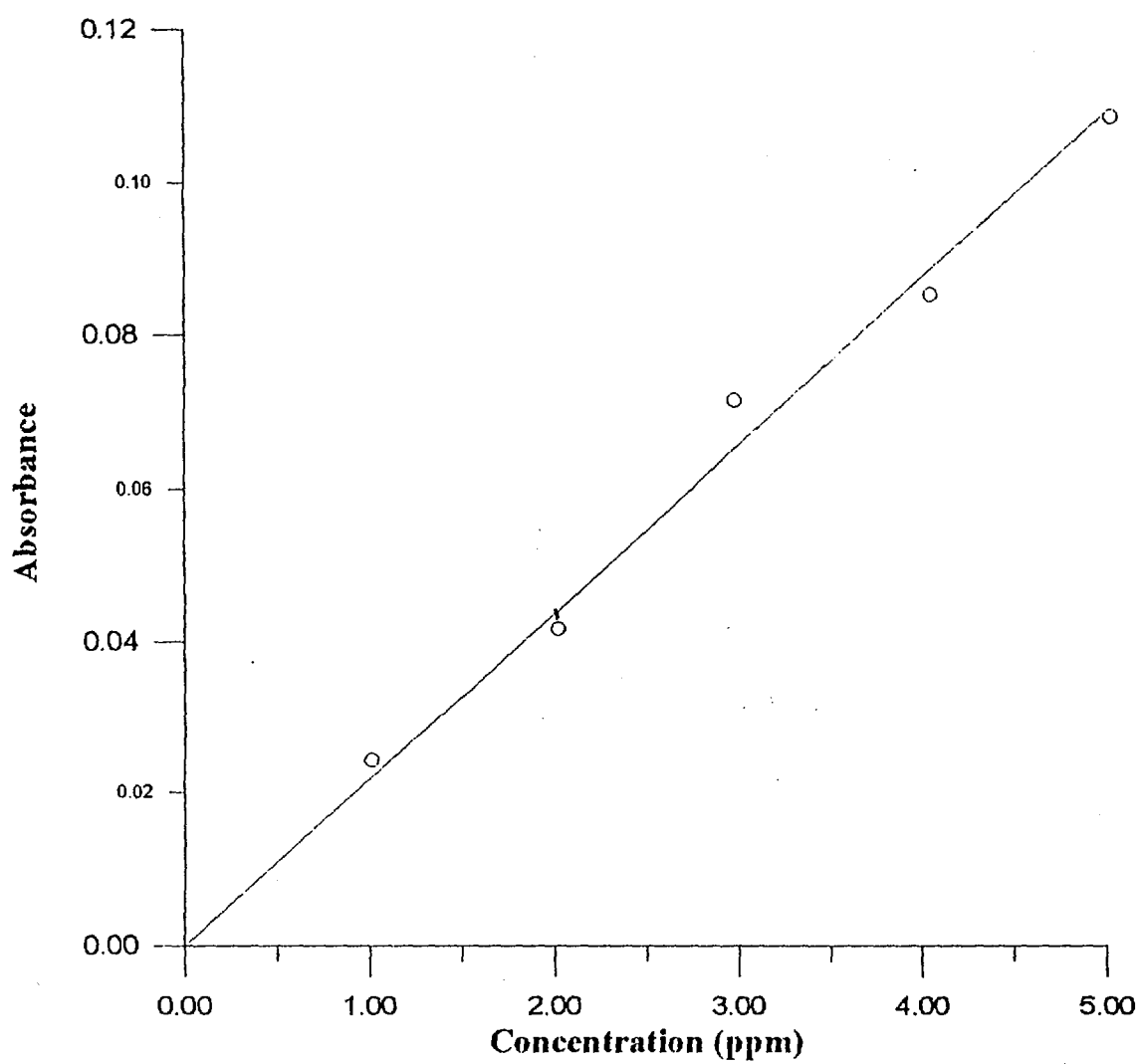
Table (23) Readings of N-phenylbutyro. H.A. for spectrophotometric determination of U(VI).

| Conc. ppm | 1 | 2 | 3 | 4 | 5 |
|------------|-------|-------|-------|-------|-------|
| Absorbance | 0.023 | 0.042 | 0.069 | 0.084 | 0.110 |

Readings of N-p-chlorophenylbutyroH.A.

Table (24): spectrophotometric determination of U(VI).

| Conc. ppm | 1 | 2 | 3 | 4 | 5 |
|------------|-------|-------|-------|-------|-------|
| Absorbance | 0.024 | 0.048 | 0.063 | 0.092 | 0.120 |



**Fig. (23): Beer's Law Curve Of N-phenylbutyrohydroxamic
Acid - U (VI) Complex**

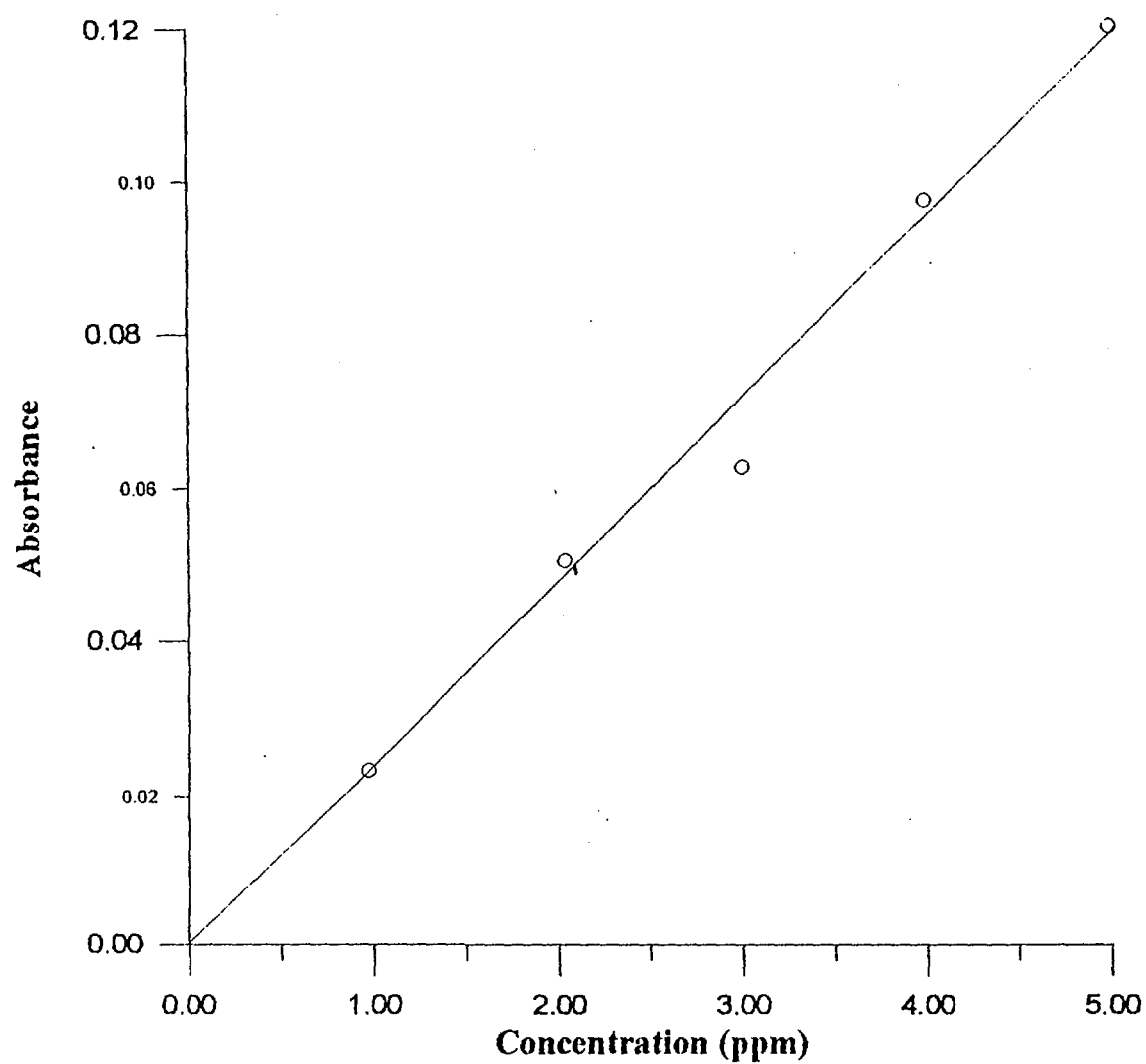


Fig. (24): Beer's Law Curve Of N-p-Cl-Phenylbutyrohydroxamic Acids- U (VI) Complex

CHAPTER THREE

DISCUSSION

CHAPTER THREE

DISCUSSION

3.1- Preparation:

Two hydroxamic acids, N-phenylbutyroxamic acid and N-p-Chlorophenylbutyroxamic acid were prepared through the coupling reaction of an equimolar quantities of acid chloride and N-aryl hydroxylamine in benzene and suspension of NaHCO_3 solution, at room temperature.

The acid chloride, prepared by reaction between butyric acid and redistilled thionyl chloride, was coupled with freshly prepared β -phenylhydroxylamine and p-chlorophenylhydroxylamine which were prepared by reduction of nitrobenzene and p-chloronitrobenzene, respectively, by zinc dust in aqueous ammonium chloride medium. The product was recrystallised from a mixture of benzene-petroleum ether ($60-80^\circ \text{C}$).

3.2- Characterization And Identification:

The two acids prepared were identified by:

Their reactions towards ferric (III) and vanadium (V) solutions which gave blood-red and deep violet colour respectively. The melting point of N-phenylbutyroxamic acid was found 80.5°C (Lit: 81.0°C), for N-p-chlorophenylbutyroxamic acid it was found 85.0°C .

The nitrogen content of the two acids had been determined by Kjeldahl method. For acid(I) it was found 7.40%, the theoretical value 7.82%. For acid(II) it was found 6.31%, the theoretical value 6.55 %. The chlorine content for acid (II) was determined gravimetrically by silver nitrate method, it was found 16.73%, theoretical value 16.62%.

The I.R. spectra for the two acids showed the most characteristics bands associated with hydroxamic acid functional groupings as in the appendix A& B.

3.3 Extraction:

Chloroform solution of the two acids were used for extraction at the transitional metal ions, Cr (VI), Mo (VI), Ti (IV) and U (VI), at different pH values

Cr (VI) in acid media forms yellow complex with two acids, chromium remains in aqueous layer was determined by the diphenylcarbazide method.

For the two acids, maximum extraction takes place at pH 1(100%). This result agrees with that obtained by Moneer⁽⁸⁸⁾ who used five substituted aryl hydroxamic acids and obtained (100%) at 3M H₂SO₄. Abdalla⁽⁸⁷⁾ used N-p-tolyl-N-benzo and N-p-tolyl-N-benzohydroxamic acids and obtained 78.32% and 52.93% at pH 1. Mohammed⁽⁸⁶⁾ obtained 77.5, 57.5 at 3M H₂SO₄ using 3 arylhydroxamic acid. So this is equal to Moneer and better than Abdalla And Mohammed.

Mo (VI) forms colourless complexes with the two acids, Mo (VI) remaining in aqueous layer was determined by the thiocyanate method. The max. extraction takes place at pH 1 93.75% with N-phenylbutyrohydroxamic acid and 73.75% with N-p-Cl-phenylbutyrohydroxamic acid. Comparing these results with that obtained by others, A/Gaffer⁽⁷⁸⁾ obtained 41.5, 42.5, 96.2 and 73.2% at pH 1 using stearo, N-phenyl stearo, oleo and N-phenyl oleo hydroxamic acid. El Mugadad⁽⁸⁰⁾ obtained 99.5% using salicylhydroxamic acid, 92.% using N-phenyl salicyl hydroxamic acid, 98% using o-methoxybenzohydroxamic acid and 100% using o-methoxybenzothiohydroxamic acid. Khalid⁽⁸¹⁾ obtained 95.1% using two substituted benzohydroxamic acid. Mohammed⁽⁸⁶⁾ extracted 94.25, 90 and 83% at pH 2 using three substituted N-phenyl benzo hydroxamic acid. Abdalla⁽⁸⁷⁾ used N-p-tolyl-N-benzo hydroxamic acid and N-p-tolyl-N-p-nitrobenzohydroxamic acid and obtained 95.4 and 94.6% at pH 1. Moneer⁽⁸⁸⁾ used 5 substituted aryl hydroxamic acid and extract > 91% at pH 1.

Ti (IV) in acidic medium form yellow complexes with two acids, Ti (IV) in aqueous layer was determined by hydrogen peroxide method. Maximum extraction of Ti (IV) with N-phenylbutyrohydroxamic acid 33.34% and 16.67% with N-p-Cl-phenylbutyrohydroxamic acid at pH 2, these values are in agreement with results of Mohamed⁽⁸⁶⁾ 21.7, 14 and 10% at pH 5 using 3 substituted aryl hydroxamic acids. Hind⁽⁸³⁾ removed 65.37 and 28.7% at 0.5 M nitric acid using hydroxamic acids driven from cotton seed oil. Abdalla⁽⁸⁷⁾ obtained 15.48 and 11.16% at pH 6 using N-p-tolyl-N-benzo hydroxamic acid and N-p-tolyl-N-p-nitrobenzo hydroxamic acid.

U (VI) forms orange complex with the two acids, U (VI) in aqueous layers was determined by the 8-hydroxyquinoline, maximum extraction occurs at pH 6, 72% for N-phenyl butyrohydroxamic acid and 76% for N-p-Cl-phenylbutyrohydroxamic acid. A/Gaffar⁽⁷⁸⁾ removed U (VI) up to 93% at pH 6 using aliphatic acids (oleo & stearo hydroxamic acids). Abd/ El razik⁽⁸²⁾ extracted 97% of uranium (VI) at pH 6 using hydroxamic acids driven from phthalic acid. Mohamed⁽⁸⁴⁾ and Abdalla⁽⁸⁷⁾ extracted 100% at pH 7 with N-aryl substituted benzohydroxamic acid.

3.4- Continuous Variation Method:

Jop⁽⁵⁷⁾ pointed that the method of continuous variation is simple and rapid for the determination of the formula of the complex.

Cr (VI) react with N-phenylbutyrohydroxamic acid and N-p-Cl-phenyl-butyrohydroxamic acid at PH 1 to give complexes with 1:2, metal: ligand ratio.

The proposed formule for the complexes are $\text{Cr}(\text{C}_{10}\text{H}_{12}\text{NO}_2)_2\text{O}_2$ & $\text{Cr}(\text{C}_{10}\text{H}_{12}\text{NClO}_2)_2\text{O}_2$ respectively also Ti (IV) give 1:2 complexes with the two ligand, the proposed formula are $\text{Ti}(\text{C}_{10}\text{H}_{12}\text{NO}_2)_2\text{O}$ and $\text{Ti}(\text{C}_{10}\text{H}_{12}\text{NO}_2\text{Cl})_2\text{O}$.

U (VI) give 1:2 complexes with two acids, the proposed formulae are $\text{U}(\text{C}_{10}\text{H}_{12}\text{NO}_2)_2\text{O}_2$ & $\text{U}(\text{C}_{10}\text{H}_{12}\text{NO}_2\text{Cl})_2\text{O}_2$.

3.5- Suitability Of The Ligands For Specrophotometric Determination Of The Metals:

The value of the slope of N-phenylbutyrohydroxamic acid -Cr (VI) complex was found to be 0.120 and N-p-Cl-phenylhydroxamic-Cr (VI) acid complex was found to

0.188 and that of diphenylcarbazide was found to be 0.69 at the same concentration range, from this fact the reagent is less sensitive for colourimetric determination for Cr (VI).

The value of the slope of two acids with Ti (IV) was found to be 0.0047 and 0.0034 in comparing those values with the values of hydrogen peroxide 0.0032 at same concentration range. The reagents are more sensitive than hydrogen peroxide, but their recovery of the metal is low.

The value of the slope of N-phenylbutyrohydroxamic acid-U (VI) complex was found to be 0.022 and N-p-Cl-phenylbutyrohydroxamic acid-U(VI) complex was found to be 0.023 and that at 8-hydroxyquinoline-U (VI) complex was found to be 0.025 at the same concentration range, from this fact the reagent is less sensitive for colourimetric determination for U (VI).

CHAPTER FOUR

REFERENCES

&

APPENDICS

REFERENCES :

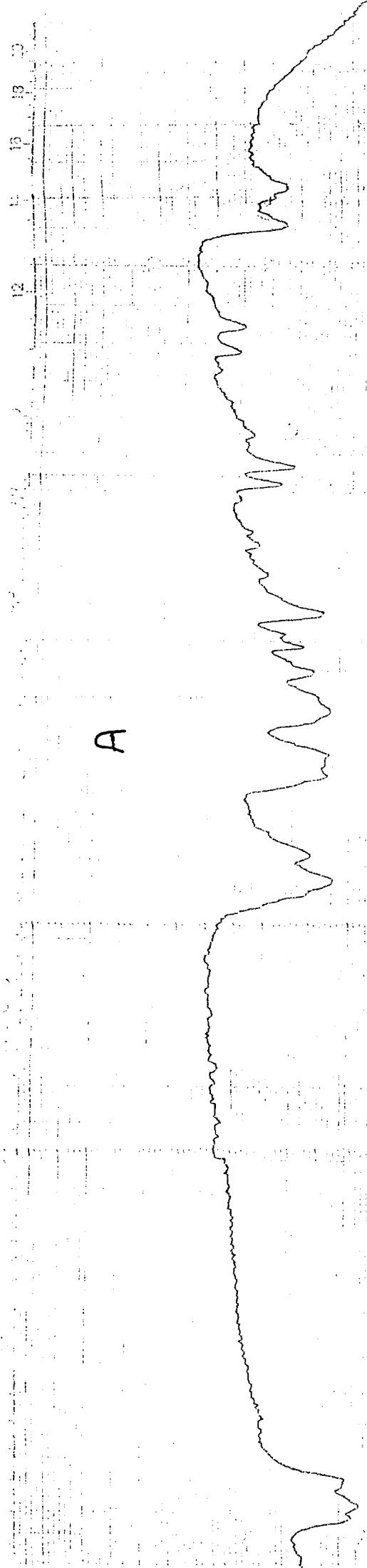
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N-phenylbutyrylhydroxamic acid

POOR QUALITY
ORIGINAL

B

POOR QUALITY
ORIGINAL

N-p-chlorophenylbutyro-
hydrazide acid

DATE PROGRAM

SCAN TIME

MULTIPLIER

TIME CONSTANT

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