EXTRACTION AND DETERMINATION OF METAL IONS BY USING THE LIGAND HAVING NITROGEN AND SULPHUR DONOR ATOMS

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By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"EXTRACTION AND DETERMINATION OF METAL IONS BY USING THE LIGAND HAVING NITROGEN AND SULPHUR DONOR ATOMS"** in partial fulfilment of the requirement for the award of the degree of Master of Philosophy submitted in the Department of Chemistry of the University is an authentic record of my own work carried out during the period from January 1998 to July 1998 under the supervision of **Dr. MALA NATH,** Associate Professor, Department of Chemistry, University of Roorkee, Roorkee.

The matter embodied in this thesis has not been submitted by me for award of any other degree.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

3-Amino-5-mercapto-1,2,4-triazole (5.0×10^{-2}M) and its schiff base with salicylaldehyde (synthesis described) have been evaluated for solvent extraction of Cu from its aqueous solution (1.0×10^{-2}M) into kerosene and toluene quantitatively and triazole (5.0×10^{-2}M) has also been used for spectrophotometric determination of copper. Extraction was found to be dependent on pH (acetate buffer of pH 4.3-5.5) and it increases with an increase in pH of the aqueous phase. Maximum extraction occurs at pH 5.30 and 5.50 using triazole and schiff base, respectively. Effect of metal ion concentration, extractant concentration, shaking time and diluent on the extraction of copper have been investigated at the pH 5.30 to optimize the conditions for maximum extraction. It has been found that extractant concentration (triazole) of 5.0×10^{-2}M is sufficient to extract 0.5×10^{-3} M of Cu(II) from its aqueous solution into kerosene at pH 5.30 ± 0.05 by using shaking time of 10 minutes . Extraction as well as back extraction behaviour of schiff base have been described in terms of its ability to form stable complex in organic phase.

The effect of diluents in the extraction process has been studied over the pH range 4.30-5.50 and their extracting capacity was found to be of the order (decreasing order) kerosene>Toluene> Chloroform = carbon tetra chloride > Xylene> Cyclohexanone.Synergistic effect of two extractants, 2,2′-bipyridine and 1,10-phenanthroline has been studied in different diluents. Back extraction studies from toluene(organic phase) were carried out by using 1.0M-3.0M of HCl. The concentration of copper in aqueous phase before and after extraction and after back extraction (with necessary dilution) has been determined by using an atomic absorption spectrophotometer in an air-acetylene flame at 324.7 nm for

Cu. The composition of the complex formed has been determined by Job's continuous variation method and molar ratio method and the stoichiometry of the complex species to be extracted was found to be most probably 1:2 (metal-to-triazole). The blue coloured complex system in H_2O obeys Beer's law in the range 0-3.0x10^{-3}M Cu (II) at λ_{max} 336.0, 348.0 and 512.0 nm and molor absorptivity is 9.9 x 10^3 L mol^{-1} cm^{-1} at 336.0 nm and 1.36x10^3 L mol^{-1} cm^{-1} at 512.0 nm.

Interfer-ence due to Fe (III) was studied by extraction- atomic absorption spectrophotometry in an air - acetylene flame at 248.3 nm. Zn (II), Co (II), Ag (I), Fe (II), Ni (II), Pb(II), K^+ and Na^+ were found to be interfer-ing .

INTRODUCTION

Transition metals, exclusively called as d-block elements, have been known because of their metallic character, ability to form stable complexes, which are further used in organometallic chemistry, catalytic activity in various chemical processes (e.g. Cu/V used in synthesis of Nylon-66), formation of large number of useful alloys (e.g. brass, bronze) and exhibiting coloring and magnetic properties.

Copper is one of the oldest metals known to man and probably the first metal employed by him for useful purposes. This name is derived from Latin "Cuprum". Copper was used as pigment and fashioned to axes, adzes and boring tools by Egyptians [1]. Copper exists in the native state and its principal ore is chalcopyrite. Copper is soft and ductile metal [2] due to which it has found wide applications in manufacturing different alloys which are hard, tenacious corrosion resistant and good conductors of heat; e.g. Brass (Cu + Zn) used in utensils and cartridges caps ; Bronze (Cu + Sn) in control valves and statue ; Phosphor bronze (Cu + Sn + P) used in electrical instruments and German Silver (Cu + Zn + Ni) used in utensils and resistance wires. Apart from this copper is used in agriculture as an insecticide. Hence, extraction of copper is very important from industrial point of view. Copper has biological importance too as copper in small amounts (4-5 mg daily) is essential for humans and its deficiency results in the inability to use iron stored in the liver, larger amounts are toxic [3] and copper is bound to proteins in the body as metalloproteins.

Due to wide applicability and importance of Copper, its selective separation is essential in analytical chemistry when either it is present with other metal ions or its concentration in samples such as environmental and waste products, in predicting the quality of finished product is to be determined. For this purpose, many extractants and chelating resins have been synthesized and employed for pre-concentration of copper by solvent-extraction method.

Chemical analysis dealt with various kinds of measurements. Sometimes determination of one component is performed in presence of other because of their selectivity. However, in most cases such a measurement is hindered by the presence of other substances in sample and therefore, for accuracy in determination a separation step known as pre-concentration step precedes the measurement. This step can be achieved by using techniques like chromatography, distillation, etc., but solvent extraction still enjoys prestigious position over these techniques because of its simplicity, ease and low operational cost (economic from country's point of view). This technique separates metal ions at both micro and macro levels.

1.1. Solvent Extraction

In modern times, particularly since the world war II, rapid modernization leads to greatly increasing variety of products and the corresponding need for making difficult separations has resulted in a rapid penetration of liquid extraction into practically every branch of the chemical process industry whether it is petroleum refining, processes related to Bio-organic molecules such as fats, oils, pharmaceutical products or inorganic chemical industries such as metal separations, metallurgical industries and so on [4].

As a result of this, solvent extraction or liquid-liquid extraction has become one of the premier separation techniques and enjoys a prestigious position among various separation techniques like precipitation, distillation sublimation, chromatography, dialysis, electro-deposition, etc. [5]. The eminence of solvent extraction over other separation techniques is due to its rapidity, convenience, sensitivity, specificity, versatility, non-destructive accessibility and low operation cost.

Solvent extraction is a technique in which a solute is transferred from one liquid phase (usually aqueous) into another liquid phase (usually organic) which is essentially immiscible with the first phase. The final stage i.e. equilibrium stage of the process is called liquid-liquid partition and the species, the distribution of which is studied, may be called the distribuend. Apart from this an extractant, a substance which reacts with distribuend by solvation, chelation, ion-pairing, ion-exchange etc. to extract it from second phase and a diluent, solvent used to either dissolve the extractant or to serve as an extracting medium also constitute a part of extraction process.

Two main factors are there which cause the distribution to favour the organic phase and they are : low affinity of the distribuend to the aqueous phase and high interaction energy of it to the organic phase.

The factors that cause a low affinity of a species for the aqueous phase are zero or low charge, large size, non-polar nature, absence of electronegative atoms at the surface, low water activity and highly ordered water structure. These factors usually also cause a high affinity for organic phase.

Distribuends may be classified broadly into "molecular" ones [which includes inorganic molecules partially covalent metal salts ($HgCl_2$), weak acids, metal chelates and solvated metal salts in low dielectric constant solvents] and " ionic " ones [Ion-Pairs consisting of large ions, metal salts of large organic anions and solvated metal salts in high dielectric constant solvents].

According to Gibb's phase rule for the distribution equilibria between two liquid phases, we have

$$V = C - P + 2 \qquad (1)$$

Where, V = Variance of the system (Number of independent variables viz. P,T, concentration)

C = Number of components

P = Number of phases

In a ternary system, if a solute is added to the binary two-phase system (two immiscible liquids) [C = 3 and P = 2], we have one variable and thus at a given temperature the concentration of the solute in one of the phases may be arbitrarily selected. Hence, at equilibrium a definite relationship must exist between the concentrations of the solute in two phases. Addition of one component adds one degree of freedom and hence concentration of solute in one phase can be selected at will. This theory from phase rule is the basis of formulation of distribution law given by Nernst and can be stated as

"A solute when brought in contact with two immiscible solvents distributes itself in them in such a way that at equilibrium the ratio of its concentration in two phases will be a constant at a particular temperature, provided no molecular association or dissociation undergoes between solute molecules in any phase."

Mathematically,

$$\mu_a = \mu_b \qquad (2)$$

where, μ_a and μ_b are chemical potentials of the solute A at equilibrium when two immiscible phases a and b are brought into contact and will depend only on temperature.

Distribution constant (coefficient) can be given as

$$K_D = \frac{\text{Concentration of solute A in solvent a}}{\text{Concentration of solute A in solvent b}} \qquad (3)$$

Equation (3) can be modified by taking distribution ratio D (or extraction coefficient E) in place of K_D, as

$$D = \frac{[Ca]_a}{[Ca]_b} \qquad (4)$$

Where, C_A = Concentration of A in all its forms as determined analytically.

Amount of solute remaining in water layer after n extractions can be given by relation

$$x_n = x_0 \left[\frac{DV}{DV + v}\right]^n \qquad (5)$$

Where, x_0 = weight of solute in V ml of aqueous solution

D = Distribution ratio between two phases viz. water and given organic solvent

n = number of extractions

v = volume of solvent (ml) taken in each extraction

In general it is assumed, that formation of uncharged molecules is a required precondition (pre-requisite) for extraction into organic solvents with their normally low dielectric constants because ionic compounds lose large amount of electrostatic solvation energy on extraction from aqueous solutions to organic solvents (an unfavourable condition).

Solvent extraction has been used predominantly for the extraction of metal salts from their aqueous solution into organic solvents. These metal salts have high solubility in aqueous media so water molecules coordinated to metal ions must be removed before carrying out the extraction and this can be done by using reagents which acts as ligands and helps in bringing metal in neutralized form more organic like [6] by forming metal chelate complexes [7] or by ion association. We can represent equilibria between principal processes taking place in solvent extraction systems as follows :

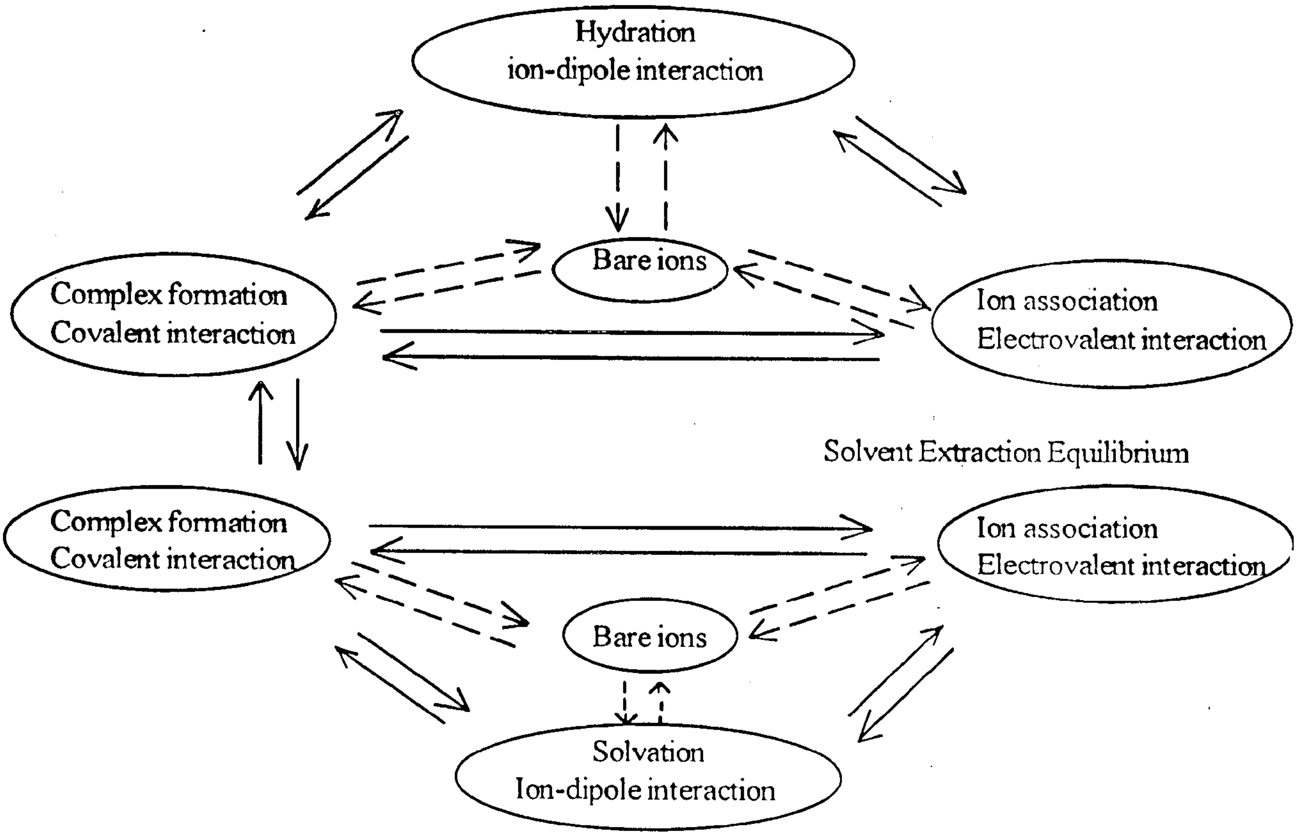


Fig. 1: Equilibria Between Principal Processes

In this figure, ion association reveals a condition where different ions are separated by solvent molecules, while complex formation is a state where ions are not separated by solvent molecules.

Significance of chelating effect and synergistic extraction has been emphasised by Vogel [8]. It has been found that the following features of the ligands affect chelate formation :

i> Basic strength of chelating group ;

ii> Nature of donor atoms in chelating group ;

iii> Ring size ;

iv> Resonance and steric effects ;

A lot of work has been done to suggest and prove the extraction of metal ion, M^{n+} with enhanced efficiency using a mixture of an acidic chelating reagent, HR, and an uncharged basic reagent, S, forming a mixed complex, MR_nS_x, which is extracted with much greater efficiency than the parent chelate (*synergism*). Pyridine and 1,10-phenanthroline can be cited as an examples.

Solvent extraction of a neutral metal chelate complex formed from a chelating resin HR according to equation

$$M^{n+} + nR^- \rightleftarrows MR_n \qquad (6)$$

can be treated quantitatively if it is assumed that the reagent and the metal complex exist as simple unassociated molecules in both phases, that solvation has least importance in extraction process and that solutes are uncharged molecules and show little deviation from ideality [8]. The distribution of metal in a given system has been proved as a function of pH alone.

Solvent extraction has been used as a pre concentration technique prior to its determination by techniques like atomic absorption spectrometry and chromatography. This technique provides a clear and simpler separation of metal ions at both micro and macro levels. Study of the extraction equilibria helps in predicting existence of various complex species in aqueous phase, in kinetics and thermodynamic aspects of chemical reactions. The basis of this technique can be extended to **reverse phase chromatographic column separation.** Solvent extraction can be employed analytically for specific separation of a specie from a mixture of species.

Extraction can be formulated in two different ways :

1> Batch extraction

Procedure in which two layers are shaken in a separating funnel so as to extract solute from one layer into the other layer, until equilibrium is attained and then making an arrangement to settle the layers completely and removing the layer containing the desired constituent.

2> Continuous extraction

This method is employed when distribution ratio is low. It is a type of counter-current extraction [5] where a continuous flow of immiscible solvent is made through the solution containing the extractable species.

A number of extraction systems have been investigated and continue to be explored for the separation of metal ion because of great potential and versatility of the technique. Based on the extraction concepts like mechanism of extraction, nature of extracted species, etc., the extraction systems have been classified. Yet one of the most convenient classification is based on types of extractants or solvents used according to basicity, polarity, dielectric constant etc. which is given by Marcus [9]. These can be grouped in the following way :

1> Inert solvents

These extract only non-polar species, such as iodine or chelates and are used also as diluents. They can be graded according to :

i> Polarity : e.g. non-polar CCl_4 and polar 1,1-dichloroethane

ii> Polarizability : e.g. benzene

iii> Hydrogen bonding ability : e.g. $CHCl_3$ and not. CCl_4

2> Basic solvents

They extract mainly by solvating either anionic metal complexes or metal ions or hydrogen ions. They are graded according to basicity, e.g. phosphine oxides R_3PO, Phosphates $(RO)_3PO$, Ketones R_2CO, Ethers R_2O, high molecular weight amines, etc.

3> Acidic extractants

They extract through cation exchange reaction, by exchanging hydrogen ions for the extracted cations. They are classed according to their acidity from thenoyltrifluoroacetone through dialkyl phosphates to carboxylic acids.

4> Chelating extractants

They extract by forming strong coordinate bonds with metals thus leading to complex or chelate formation. They may contain zero to several displaceable hydrogen ions. They may be neutral or charged and may be more basic or more acidic, e.g., 8-hydroxyquinoline and thenoyltrifluoroacetone, respectively.

5> Ionic extractants

Depending upon the dielectric constant of the diluent, these occur either as dissociated ions or undissociated electrolytes. Active extractant species may be either the cation (e.g. tetraphenyl arsonium) or the anion (e.g. tetraphenyl boride).

1.2. Literature Review

A comprehensive review of a decade and a half long existing literature available on the solvent extraction and spectrophotometric and atomic absorption spectrometry determination of Cu(II) using various extractants, and synthesis of Schiff bases and their application for extractive-spectrophotometric determination has been presented in the following pages. For a greater look into extracting behaviour of various extractants and sake of simplicity it has been divided among various extractants on the basis of the basic skeleton present in their molecules.

1.2.1. Extractants containing azo group

It has been investigated that the compounds containing azo group attached to the aromatic acids or phenols on aromatic hydrocarbons such as 4-dodecyl-6-(2-thiazolylazo)- resorcinol, 1-(2-pyridylazo)-2-naphthol and 2-(2-hydroxynaphthylazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole were used for extractive and spectrophotometric determination of Cu(II) in the range 500-540 nm into the solvents like ethyl methyl ketone, isobutyl methyl ketone, 1,2-dichloroethane, CCl_4 and $CHCl_3$ in the pH range 2.8-14.0 with average recovery 99-105% and coefficient of variation 4.6-4.8% [10-13].

Katami et al. [14] devised a spectrophotometric method for the extraction of Cu(II) into dimethylformamide and acetone using 2-(2-benzothiazolylazo)-5-dimethylamino benzoic acid by measuring the absorbance of the complex at 650 nm. Beer's law was obeyed for 0-16 μg of Cu and Sandell's sensitivity was 1.1 ng cm^{-2}.

Shinde [15] formulated a method for the extraction of Cu(II) into mesityl oxide and then back extraction into H_2O followed by the addition of 4-(2-pyridylazo) resorcinol and measuring the absorbance of complex at 540 nm.

Saran et al. [16] proposed a method for the extractive atomic absorption spectrophotometric determination of Cu(II) in the presence of Fe, Co, Ni using

5-(2′-carbomethoxyphenyl)azo-8-quinolinol in acetone as a complexing agent into isobutyl methyl ketone at pH 5.5-6.5. Organic layer was used for the determination of 20 μgl^{-1} of metal ion, for which the coefficient of variation was 2-7% (n = 10). Recovery was generally >95%. Detection limit was from 0.07-0.38 μgl^{-1}. Method was applied to drinking water or bore well water.

Ge et al. [17] described a method for the spectrophotometric determination of Cu(II) with ligand-exchange extraction method which involves extraction into $CHCl_3$ at pH 9.2 in the presence of EDTA/ammonium citrate in H_2O using diethyldithiocarbamate followed by treatment of organic layer with ethanolic 2-(5-bromo-2-pyridyl-azo)-5-diethyl-aminophenol in the presence of buffer of pH 9.2 and cetylpyridium bromide. Absorbance of organic phase was measured at 520 nm (ϵ = 122000). Beer's law was obeyed for 0.2-10 μg Cu/10 ml of solution. Method was applied to analyse food, water and urine samples.

1.2.2. Thiosemicarbazones as extractants

It has been observed that in the recent years very few thiosemicarbazones were used as extractants for determination of Cu(II). Some thiosemicarbazones such as 2′,4′-dihydroxyacetophenone thiosemicarbazone, anisaldehyde 4-phenyl-3-thiosemicarbazone, etc. are used for spectrophotometric determination in the range 350-450 nm (ϵ = 13,000-45,000) after extracting Cu(II) into solvents like $CHCl_3$, isobutyl methyl ketone, ethyl acetate, etc. in the pH range 3.0-7.5 with Beer's law obeyed in the range 0.1-5.5 $\mu g\ ml^{-1}$ of Cu [18,19].

Reddy and Reddy [20] determined Cu(II) in presence of Fe(III) and Ni(II) by extractive spectrophotometric determination of organic layer (butanol) at 380 nm vs. a reagent blank using salicylaldehyde thiosemicarbazone as extractant in the pH range 6.5-7.5. Beer's law was obeyed for 0.3-3.5 ppm of Cu and coefficient of variation was 1.42.

Lee et al. [21] formulated a method for extraction atomic absorption spectrophotometric determination of Cu(II) in presence of Co, Cd, Mn, Hg, etc. with 4-phenyl-3-thiosemicarbazonopicolinaldehyde into $CHCl_3$. Detection limit was reported to be 0.5-7.5 μg/ml.

1.2.3. Hydroxamic acids as complexation species

Several species of hydroxamic acids such as derivatives of N-phenylbenzohydroxamic acid [22], N-phenylalkanohydroxamic acids [23], etc. have been used for the solvent extraction of Cu(II) into $CHCl_3$, CCl_4, etc. followed by atomic absorption spectrophotometric determination of aqueous phase in the pH range 3.0-9.5. Salinas et al. [24] used substituted benzohydroxamic acid in the pH range 1.0-9.0 to study the extraction of Cu(II) and Co(II) into solvents like $CHCl_3$, isoamyl alcohol, toluene and adogen 464.

1.2.4. Extractants containing triazine group

Compounds containing reactive triazine moeity in their molecule such as triazen N-oxide [25] have been used in developing an extractive-spectrophotometric determination of Cu(II) into $CHCl_3$ in the pH range 7.0-10.6. Beer's law was obeyed for 0.25-4.7 ppm of Cu with Sandell's sensitivity 5.3 ng cm^{-2}. Standard deviations for 2 ppm (n = 16) is 0.22%.

Toral and Richter [26] has developed a method for simultaneous determination of Cu and Fe by solvent extraction and first derivative spectrophotometry using 5-phenyl-3-(4-phenyl-2-pyridinyl)-1,2,4-triazine in dichloroethane. Spectra was recorded from 400-650 nm. Calibration graphs were linear for 20-2500 ng/ml of Cu with detection limit 17 ng/ml. RSD was reported to be 2.1%. Method was applied to well water.

1.2.5. Extractants containing sulphur atom

A number of compounds having sulphur atom moeity in their molecule has been investigated in the literature for the extractive and spectrophotometric determination of Cu(II) either independently or in presence of other metal ions. To have a clear view of various extractants used they can be subdivided into following classes:

1.2.5.1. Carbodithioates

Several substituted carbodithioates and carbodithioic acids have been investigated for extractive spectrophotometric determination of Cu(II) [27-31]. These includes pyrrolidine-1-carbodithioate and their ammonium salts **(I)**,O,O-diethyl phosphorodithioate **(II)**, pyrrolidine-1-carbodithioic acid**(III)** and hexahydroazepinium hexahydroazepine-1-carbodithioate **(IV)**. Of these, **(II)** has been used for the extraction of Cu(II) into hexane using H_2O_2 at pH 0-6.0 followed by spectrophotometric determination at 419 nm ; **(III)** has been used for extraction into isobutyl methyl ketone at pH 4.0 - 5.5 followed by atomic absorption spectrophotometric determination of organic phase, detection limit was 0.4 ppb in natural waters ; **(IV)** has been investigated for extraction in $CHCl_3$ at pH 8.0 followed by spectrophotometric determination at 260 nm with coefficient of variation 1.2-5.9% in the range 1.9 - 29.7 ppm of Cu(II) in citrus leaves and rice flour;**(I)** has been investigated for extraction of Cu(II) and Ni(II) into isobutyl methyl ketone, di-isobutyl ketone and 1,1,1-trichloroethane followed by atomic absorption spectrophotometric determination of organic phase with detection limit 0.01-0.66 μg of Cu, Coefficient of variation ≤ 7.2% (n = 6-13), recoveries 94.8-118% and calibration plot rectilinear for ≥10 $\mu g l^{-1}$ of water sample and 40 $\mu g\ g^{-1}$ of titanium metals. Murakami and Takada [31] formulated a method to compare the extracting capability of isobutyl methyl ketone and di-isobutyl ketone using (I) and measuring the absorbance of organic phase at 435 nm.

1.2.5.2. Dithiocarbamate

Substituted dithiocarbamates such as ethylammonium diethyl-and sodium diethyldithiocarbamates have been investigated for extraction of Cu(II) in presence of Co, Ni, Pb into isobutyl methyl ketone and di-isobutyl ketone at pH 3.0-5.0 followed by atomic absorption spectrophotometric determination of 2-5 ng of Cu with coefficient of variation 0.2-3.2% and recoveries ranging from 95.3 to 102.6% [32].

Popova et al. [33] formulated a method for the extraction of Cu(II) into isobutyl methyl ketone with pyrrolidinedithiocarbamate in presence of Ni, Zn, Pd followed by flame atomic-absorption spectrometric determination.

1.2.5.3. Thiocarbamide

Phenylthiourea has been investigated from extraction point of view. Patil et al. [34] developed a method for the extraction of Cu(II) using 1-phenyl-3-benzoyl thiocarbamide into $CHCl_3$ at pH 5.8-6.3 followed by spectrophotometric determination at 380 nm. Beer's law was obeyed in the range 0.3-6.0 ppm of Cu in $CHCl_3$ solution.

Ide and Takagi [35] formulated a method for the selective extraction of Cu(II) in presence of Hg(II), Pb(II) using N-(2-butylthiophenyl)-

N′-phenylthiourea into chlorobenzene at low pH. Synergistic effect of 4-benzylpyridine and trioctylphosphine oxide was found to be small.

1.2.5.4. Dithizone

Dithizones have been employed by researchers for studying the extraction behaviour in different solvents and also for extraction and determination of Cu(II) by first derivative spectrophotometry in presence of Pb(II) and Hg(II) from marine sediment samples.

Itabashi et al. [36] studied the effect of presence of acetone in the extraction of Cu(II) as Cu-dithizonato complex from aqueous acetone. Logarithm of extraction constant (K_{ex}) was 7.56 which was larger than those obtained in absence of acetone (explained on the basis of HSAB principle). Increased K_{ex} value may be attributable to the increase in hardness of dithizone when acetone is added.

Kiwan et al. [37] studied acidity constant, partition coefficient of dihalo-2,2′-dimethyldithizone for extracting Cu(II) into $CHCl_3$ or CCl_4. Extraction behaviour of tetra halo dithizone complexes relative to dihalodimethyl-dithizone and effect of pH on extraction have also been investigated.

1.2.5.5. Heterocyclic dithiophosphates

Heterocyclic dithiophosphates having mercapto group such as 2-mercapto-4,7-dimethyl-1,3,2-dioxaphosphopane-2-thione have been used for spectrophotometric determination of Cu(II) at 422 nm vs. a reagent blank after extraction into toluene. Beer's law was obeyed from 0.5-4.0 $\mu g\ ml^{-1}$ of Cu(II). Au(III) and Hg(II) interferred [38].

1.2.5.6. Thioethers

Cyclic and acyclic tetra thioethers and thiacrown ethers have been used exclusively for the extraction and spectrophotometric determination of Cu(II) [39-41]. Some of them are hydroxy phenyl azo derivative of benzo-2,5,9,12-tetra thia-cyclopentadecane (V), dithiahexadecane(VI),p-nitrophenylazo derivative of bisthiacrown, tetrathiacyclotetradecane(VII), tetrathiapentadecane(VIII) and hexathiacyclooctadecane (IX) which have been used for extraction of Cu(II) into 1,2-dichloroethane exclusively followed by atomic absorption spectrophotometric determination of aqueous phase. Of these, (V) and (VI) (both thioethers) have been used for extraction into toluene and 1,2-dichloroethane in combination with reducing agent hydroxylammonium sulphate along with a possibility for back extraction ; (VII) and (IX) have been used to analyze the effect of counter anion (tetra bromophenolphthalein ethyl ester as counter ion) at pH > 8.0 for the extraction of 50μM-Cu(II) into 1,2-dichloroethane followed by spectrophotometric determination of extract at 608 nm (molar absorptivity, ϵ = 88,000) alongwith extraction efficiency of > 99% ; (VII) and (VIII) were used for extraction of Cu(II) into 1,2-dichloroethane in presence of borate buffer followed by atomic absorption spectrophotometric determination of organic as well as aqueous phase.

Saito et al. [42] have synthesized thiacrown ethers with pendant carboxylic acids and evaluated them as extraction reagent for metal ions in comparision to neutral thiacrown compound. Extraction of ≈ 91.5% was achieved using 1,2-dichloroethane in presence of picrate ion (for ion formation) at pH 7.0. Extractibility of Cu(II) with tetrathiacyclotetra-dec-1-oxy hexanoic acid into various solvents has been found to be in the order benzene = 1-octanol > 1,2-dichloroethane.

Abe et al. [43] formulated a method for liquid-liquid extraction and atomic absorption spectrophotometric determination of Cu(II) as ion-paired complexes at pH 8.3 (borate buffer) with 5-methyl-1,2-bis-(2-thienyl)-2,5,8,11-tetrathiadodecane (containing polythioether and triphenylmethane dye anion) in nitropropane in presence of tetrabromophenolphthalein ethyl ester.

1.2.5.7. Thio-oxamide

Puri et al. [44] devised a method for extraction of 2-9 μg of Cu with rubenate [dithio-oxamide] at pH 3.8 (acetate buffer) onto microcrystalline naphthalene in acetone. After filtration of precipitate, it was dissolved in DMF-thiourea-HNO_3 and determination of Cu(II) was carried out by absorption spectrophotometry in air-acetylene flame at 324.7 nm. Coefficient of variation at 45 μg was 1.8% (n = 8). Method was applied to alloys water and human hair samples.

1.2.5.8. Thiuram

Ilyas and Joshi [45] formulated a procedure involving micro determination of Cu(II) by extractive spectrophotometric method with tetramethylthiuram monosulphide in acetone as an extractant and toluene as an extracting solvent at pH 4.0 using acetate buffer. Absorbance were measured at 430 nm vs. a reagent blank. Beer's law was obeyed for 0.2-5.0 $\mu g\ ml^{-1}$ of Cu. Method was applied to the analysis of alloys and chalcopyrite ores.

1.2.6. Extractants possessing carbonyl or their derivatives skeleton

Literature survey suggests the extensive use of extractants possessing carbonyl as basic skeleton for the extraction and spectrophotometric determination of Cu(II). Various types of such groups can be subdivided into following groups:

1.2.6.1. Oxime

Derivatives of acetophenone oxime have been evaluated for extractive spectrophotometric determination of Cu(II) in the pH range 3.5 to 5.5 into $CHCl_3$, cyclohexanone and acetone-benzene in the presence of synergists like diethylamine, pyridine and its methyl derivatives which enhances extraction and ϵ values of complexes at 390 nm [46, 47]. Methods were applied for Cu(II) determination in German Silver alloy.

Egashira et al . [48] synthesized compounds having hydroxyoxime moieties and used them for extraction of Cu from acidic sulphate solution forming 1:2 (metal-to ligand) complex.

Reddy and Hussain [49] formulated a method for 10-60 μg of Cu(II) extraction with 2-hydroxy-1-acetonaphthone oxime into isobutyl methyl ketone at pH 4.0 followed by spectrophotometric determination of organic phase at 370 nm. Beer's law was obeyed for 20 to 60 μg of Cu(II). Method was applied to brass and chalcopyrites.

Derivative of salicylaldoxime has been used for extraction and spectrophotometric determination of Cu(II) into $CHCl_3$ in aluminium alloys [50].

1.2.6.2 Ketones

β-Diketones (LIX54) and their fluorinated derivatives (LIX51) have been used for extraction of Cu(II) into isobutyl methyl ketone in the pH range 3.0 - 9.0 [51,52].

β-Diketone derivatives [53,54] such as trifluoro methylhexane and tetra-azacyclotetradecane have been used for extraction into H_2SO_4 and p-xylene at pH 4.0 - 6.0 followed by atomic absorption spectrophotometric determination using air - acetylene flame at 324.7 nm.

Thenoyltrifluoroacetone and their thio derivatives and benzoyltrifluoroacetone have been used for extraction of Cu(II) selectively into CCl_4, isobutyl methyl ketone in presence of Co(II), Ni(II), Pd(II), ClO_4^-, SCN^- either as an extractant or as a synergist in conjugation with TOPO-cyclohexane and substituted aliphatic ketones in highly acidic medium followed by atomic absorption spectrophotometric determination [55-57].

Ueda et al. [58] used mercapto thienyl ketone derivative in conjugation with TOPO in cyclohexane as synergic extraction solution using borate buffer for extractive atomic absorption Spectrophotometric determination of organic phase with a detection limit from several ngl^{-1} to 0.1 ngl^{-1}.

1.2.6.3. Hydrazone

Hydrazones [59,60] such as pyridyl amidino-, chlorobenzoyl-, have been in use for extraction and atomic absorption spectrophotometric determination of Cu(II) along with Ag, Au, Ni, Zn, Co, Pd etc. into isobutyl methyl ketone and xylene in the pH range 6.0- 8.0 using air - acetylene flame at 324.8 nm. Coefficient of variation was <5% (n = 7) in determining 1.0 - 5.0 μg of Cu. These are also subjected to spectrophotometric determination at 440 nm with recovery of 106.33%.

Siles Cordero et al. [61] have synthesized thiocarbonohydrazones and prove them to be effective reagents for separation and pre-concentration of Cu(II) before atomic absorption spectrophotometric determination by extracting yellow complexes into isobutyl methyl ketone.

1.2.6.4 Carbazones

Diphenylcarbazones and their derivatives [62] have been used for extractive- spectrophotometric determination of Cu (II) into $CHCl_3$ and isobutyl methyl ketone at pH 5.0-6.0 and measuring absorbance at 540 nm (ε =60,000 -1,50000) vs. a reagent blank. Recovery was 90-104% with coefficient of variation 1.3-1.4%. Beer's law was obeyed for 0.4 - 1.40 μg of Cu and Sandell sensitivity was 1ng cm^{-2}.

1.2.7. Phosphorus containing extractants

A few of the organic molecules containing phosphorus group were used as an extractant. bis - (2- ethyl hexyl) hydrogen phosphate has been used for extraction of Cu (II) into organic phase [63]. Alkyl phosphoric acid and neutral organophosphorus extractants were used to study synergistic and antagonistic effect and mechanism of enhanced extraction [64]. Derivatives of phosphinic acids such as ethyl hexyl derivative have been investigated for extraction of Cu(II) alongwith Fe (III) , Zn (II), Co(II) etc. into heptane as a function of pH and concentration of extractant followed by spectrometric determination of aqueous phase [65]. Organophosphorus reagents were used as extractants by Lobana et al [66]. They investigated synergic effect of triphenylphosphine oxide on the extraction of Cu (II) with 8- hydroxyquinoline in $CHCl_3$ with subsequent spectrophotometric determination.

Atanasova and Shishkov [67] employed mercapto derivative of dioxaphosphorinane sulfide for extraction of Cu (II) in molybdenum concentrates into toluene followed by measurement of absorbance of organic phase at 420 nm vs. a reagent blank. For < 10% of Cu, relative error was reported to be < 2.2%.

1.2.8 Acids as extractants

Substituted naphthalene-and quinoline-sulphonic acids have been used to extract Cu (II) into organic phase such as $CH_2Cl_2$and $CHCl_3$ in presence of zephiramine chloride and tribenzylamine, respectively; organic phase was then subjected to measure absorbance when Beer's law was obeyed for ≤ 8 μgml^{-1} of Cu; extracted species was found to contain Cu (II) - sulphonic acid- benzylamine in the ratio 1:2:2 [68].

Substituted heterocyclic -2- carboxylic acids which are linked via ether or sulphide bonds have been used for extraction of Cu (II) from aqueous solution into $CHCL_3$ in the pH range 1.5-4.0 [69].

Moriya et al. [70] investigated and compared the extraction behaviour of Cu (II) with adamantane carboxylic acid with that of pivalic acid and cyclohexanecarboxylic acid. Concentration of Cu (II) in aqueous phase and in organic phase (after back extraction with dil. HNO_3) were measured colourimetrically with chromazurol S.

Yamada et al .[71] investigated extraction of Cu (II) by benzoic acid using octanol/benzene and octanone/benzene solvents and suggested the mechanism responsible for all extraction systems .They also suggested that mixed solvents with certin composition were shown to be superior to $CHCl_3$ for benzoic acid extraction of Cu(II).

Aliphatic carboxylates have been examined for extraction into hexane medium in the pH range 1.0-9.0. Phenyl acetic acid has been used for extraction of Cu (II) into benzene or n-octanol and was proved superior to other carboxylic acids such as decanoic, hexanoic , pivalic, benzoic acids because of dimerization of copper (II) carboxylate [72].

Apart from these acids resin acids (abietic acid) have also been used by some workers [73] into toluene at pH 5.0-5.5 (acetate buffer) followed by back stripping using H_2SO_4.

1.2.9. Dyes as extractants

Several classes of dyes such as ethyl violet, Eriochrome black T and triphenylmethane have been utilized by various workers for extractive spectrophotometric determination of Cu (II) [74,75] at pH 5.0 using toluene, benzene, chlorobenzene and xylene as extracting solvents and measuring absorbance at 550-615 nm (ε = 26100 - 82000). Beer's law was obeyed for upto 2-14 μg/ml of Cu and detection limit was 0.03 μg/ml. RSD (n=6) at 0.4 and 1.6 μg/ml were 4.1 and 1.0 %, respectively. Methods were applicable for analyzing Cu in alloys .

Yan et al. [76] proposed a method for the extraction of Cu (II) into $CHCl_3$ with neocuproine and eosine Y (C.I. Acid Red 87) followed by measurement of absorbance spectrophotometrically at 544 nm (ε = 68,300). Beer's law was obeyed up to 1 μg ml^{-1} of Cu. Method was applied for determination of trace Cu in chinese drugs.

1.2.10. Extractants containing fused polynuclear hydrocarbon skeleton

Extractants having phenanthrene as basic skeleton were used as their derivatives dimethyl-and diphenyl-for extraction into 1,2- dichloroethane and ethyl acetate at pH 4.5-5.0 followed by catalytic determination by measuring absorbance at 548 nm. Calibration graph was rectilinear for $\leq$ 30 ng ml^{-1} of Cu. The detection and quantitation limits were 1.4 and 4.7 ng ml^{-1}, respectively .

Method was applied to the determination of Cu in certified mussel and marine sediment samples [77].

1.2.11 Extractants containing aromatic alcohols as basic structural unit

Thieneylideneamino- and amino-2-nitroso- phenols in presence of zephiramine were proved to be good extractants for extracting Cu (II) at pH 8.5-12.0 into $CHCl_3$. Absorbance of the extract was measured at 450 nm (ε = 64,000). Beer's law was obeyed from 0.05 -1.30 μg ml^{-1} of Cu. Method was applied for determination of Cu (II) in serum, powdered milk, iron , steel and aluminium alloys [78,79].

Quinolyl and their derivatives viz. bi-and malon amide were used for extraction of Cu (II) into dichloroethane and $CHCl_3$ at pH 6.2 followed by measurement of absorbance at 550 nm. Calibration graphs were rectilinear from 0.4-3.0 ppm of Cu with coefficient of variation <2.7%[80].

Sarkar et al. [81] formulated a method for extracting Cu (II) into $CHCl_3$ using 4- nitrosoresorcinol as extractant in presence of pyridine and measuring absorbance at 365 nm vs. a reagent blank (ε=2100). Beer's law was obeyed for 1-100 ppm of Cu.

1.2.12. Amines and their derivatives as extractants

Trioctylamine (an aliphatic amine) has been employed as an extractant for extraction of Cu (II) into butyl acetate followed by an atomic absorption spectrophotometric determination at 324.8 nm with an air - acetylene flame. Sensitivity of the procedure was 0.03 μM with limit of detection 0.05 μM and Coefficient of variation 0.9%. Recoveries from the method were 90-94% [82].

N-Substituted nitrosohydroxylamine was used for the extraction of Cu (II) into isobutyl methyl ketone and an atomic absorption spectrophotometric determination of extract with detection limit 4.6 μg l^{-1} and precision of ±2.1% [83].

Amines and quaternary ammonium salts like adogens in presence of alizarin have been studied as an extractant for Cu (II) into xylene or toluene as well as synergist. Concentration can be determined both by an atomic absorption or UV-Visible spectrophotometry [84]. Substituted sulphonamides proved to be good extractants independently as well as in presence of synergist like adogen or phenanthroline for extracting Cu (II) into toluene at pH ~ 3.8. Absorption maxima comes at 374 nm [85]. Method was applied for the determination of Zn, Ni, Co, etc.

Inokuma et al. [86] have analyzed aminimide for the extraction of Cu (II) from its nitrate solution into dichloromethane at pH 5.3 and then analyzing organic layer by an atomic absorption spectrophotometry

Amido-podands such as ether diamide, ether carboxylic acid-amide and N-alkylimino di-acetamide has been employed by stephan et al. [87] for liquid-liquid extraction of Cu (II).

Hirayama et al. [88] have devised a procedure for ion-pair extraction of Cu (II) into nitrobenzene followed by atomic absorption spectrophotometric determination of organic phase after back extraction into HNO_3 using ethylene -diamine derivative such as tetrakis(1′-pyrazolylmethyl)-1,2-diaminoethane(tpzen), tetrakis(3′,5′-dimethylpyrazol-1′-ylmethyl) -1,2-diaminoethane (Me_8tpzen)etc.

1.2.13. Extractants having heterocyclic moeity as basic skeleton

A number of heterocyclic compounds containing quinoline and isoquinoline as basic structural unit have been investigated by workers for extractive spectrophotometric determination of Cu (II) [89-91]. 8-hydroxyquinoline has been used extensively for extraction into $CHCl_3$ and CCl_4 in the pH range 1.0-3.5 and measuring the absorbance of organic layer at 410 nm with detection limit of 0.4 ppb, coefficient of variation <3% and RSD (n=6) as 11.1% at 0.4 ng/l. Derivative of imidazolylisoquinoline was proposed for extractive - photometric determination of Cu (II) into $CHCl_3$ at pH 7.0-8.5, λ_{max} = 470 nm (ε=40,000) for 0.6-18 μg ml^{-1} Cu.

Heterocyclic bases such as pyridine, picoline and collidine and their derivatives have been investigated for extraction of Cu (II) into toluene or $CHCl_3$ in the pH range 2.0-9.0 with 100% recovery from aqueous solution, Beer's law was obeyed from 5-50 ppm of Cu. Also these bases have been employed in conjugation with trifluoroacetylacetone for synergistic extraction at pH 4.45 and measuring absorbance at 325 nm for analysis of alloys, environmental and pharmaceutical samples in presence of Co (II) and Ni (II) [92].

Pyridine alongwith pyrimidine-2- thiol was employed by kuchekar et al. [93] for synergic extraction of Cu(II) into $CHCl_3$ at pH 5.0 and spectrophotometric determination of organic phase at 400 nm (ε=11,600). Beer's law was obeyed in the range 5-70 μg of Cu and sandell sensitivity was 5.5 ng cm^{-2}. Method was applied to the analysis of alloys, plants and drugs.

Pyrrolidinone in the presence of bromopyrogallol red has been used for extractive-spectrophotometric determination of Cu(II) by Sun et al. [94].

1.2.14. Schiff base as extractants

A very few of macrocyclic schiff bases containing diamine, bis-phenol A, phenol, thiophene or tetra-aza groups or their homologues have been investigated for solvent extraction and spectrophotometric determination of Cu (II).

Zolotov et al. [95] proposed a method for extractive-spectrophotometric determination of Cu (II) at λ_{max} = 455 nm (ε=12,500) at pH 5.6 (acetate buffer) using N,N'-[2,2'-(ethylenedi-imino)di-benzylidene] ethylenediamine and their methylene diamine homologues as extractant into $CHCl_3$ as extracting solvent.

Tetra-aza macrocyclic schiff base ligand synthesized by reaction of a benzoxadiazole and a tetra-azacyclotetradecane was used as spectrophotometric determination of Cu (II) by flow injection analysis [96].

Shigeki et al. [97] have synthesized macrocyclic schiff bases containing thiophene or phenol subunit and tested them as ion-pair extractants for selective extraction of Cu (II) from weakly acidic medium into nitrobenzene. They suggested that increased percent of extraction is due to the enhanced stability of metal complexes because of the presence of phenol group. They also compared the extractability of metals as complexes between cyclic and acyclic tetra-aza schiff base.

Acyclic and macrocyclic schiff bases containing bisphenol A subunit were synthesized and evaluated for liquid- liquid extraction of Cu (II) in presence of Mn (II) and Zn (II) into nitrobenzene in the pH range 4-10 and atomic absorption spectrophotometric determination of metal ion in both phases [98].

Heteroaromatic schiff bases of salicylaldehyde and aminopyridine were evaluated for solvent extraction and spectrophotometric determination of Cu (II) [99]. Cu (II) was extracted into $CHCl_3$ at pH 6.0 in presence of Mn (II), Fe (III), Ni (II), Co (II) and Cr.(III). Calibration graphs were linear for 0.3-6.0 μg/ml of Cu when N,N'-bis-(salicylidene) - 2,3-pyridinediamine was used as extractant and for 0.5-10.0 μg/ ml of Cu when 2-(2-amino-4-methoxymethyl -6-methyl-3- pyridylmethyliminomethyl) phenol was used as extractant and RSD for 1.8 and 2.4 μg/ml Cu (II) were 1.6% (n=9) and 1.1 % (n=6), respectively.

1.2.15. Pyrazol containing extractants

Substituted phenyl pyrazol-5-one has been used for solvent extraction of Cu (II) at pH 2.5 into isobutyl methyl ketone followed by atomic absorption spectrophotometric determination with coefficient of variation of 2.1% [100].

Grandmont el al. [101] have studied the extraction capability of pyrazol-oyl benzene and alkanes in pH range 0.8-3.0 and extraction efficiency of 1,2-dichloroethane with that of $CHCl_3$.

Apart from the use of extractant for extraction and spectrophotometric determination few literature is also available showing pre-concentration and atomic absorption spectrometric determination of Cu (II) in presence of other metal ions [102-104]. Extracting solvents used were mainly isobutyl methyl ketone in the pH range 3.0-9.0. Atomic absorption spectrophotometric determination was carried out in an air-acetylene flame at 324.7 nm. Detection limit was ≈ 0.5 ppm -1.5 ppm of Cu. Calibration graphs were rectilinear for 0-2.5 $\mu g\ ml^{-1}$ of Cu. Recoveries were ranging from 97-99 %.

1.3 Formulation of the Problem

A critical review of a decade and a half long literature available indicates that immense work has been done on the solvent extraction of metal ions by using thiosemicarbazones, hydroxamic acids, compounds containing sulphur atom, ketones and their derivatives, acids, dyes and compounds containing heterocyclic skeleton followed by spectrophotometric determination of Cu (II) from its aqueous solution.

A very few extractants containing heterocyclic ring as well as S and N donor atoms have been used for the solvent extraction and spectrophotometric determination of Cu (II) in trace amounts by an atomic absorption spectrophotometry.

Therefore, it was considered interesting and challenging to use the compounds containing S and N donor atoms as an extractant for the extraction and atomic absorption spectrophotometric determination of Cu (II) in presence of some diverse ions, and to synthesize Schiff bases of such an extractant and use them to study their extraction behaviour towards extraction of Cu (II) form its solution with or without the presence of other metal ions or salts.

EXPERIMENTAL SECTION

2.1 MATERIALS

Metal salts, diluents for carrying out extraction and the salts and reagents used under present investigation are tabulated in Table 1

Table 1: Make and grades of various reagents used.

S.No.	Chemical/Solvent	Grade	Make
1.	Copper chloride ($CuCl_2.2H_2O$)	Extra pure	E.Merck
2.	Ferric chloride ($FeCl_3$anhydrous)	L.R.	C.D.H
3.	3-Amino-5-mercapto-1,2,4-triazole	Extra pure	E.Merck
4.	Borax	L.R.	S.D.Fine Chem Ltd.
5.	Potassium hydrogen Phthalate	A.R.	Glaxo
6.	Sodium acetate	Extra pure	E.Merck
7.	Acetic acid	G.R.	E.Merck
8.	Potassium dihydrogen phosphate	G.R.	Sarabhai Chemical
9.	Sodium hydroxide	G.R.	E.Merck
10.	Barium Chloride ($BaCl_2.2H_2O$)	L.R.	Glaxo
11.	Cobalt nitrate ($Co(NO_3)_2 6H_2O$)	A.R.	BDH laboratory
12.	Potassium chloride (KCl)	Extra pure	E.Merck
13.	Zinc Sulphate ($ZnSO_4$)	Extra pure	E.Merck
14.	Ferrous ammonium sulphate	G.R.	Loba-chemie Indo-Australian Co.
15.	Nickel sulphate($NiSO_4.H_2O$)	A.R.	Samir Tech chem Indus
16.	Lead nitrate ($Pb(NO_3)_2$)	Extra pure	E.Merck
17.	Silver nitrate ($AgNO_3$)	A.R.	Qualigens

Contd....

18.	Sodium dihydrogen phosphate (NaH_2PO_4)	-	-
19.	Salicylaldehyde	Extra pure	E.Merck
20.	2,2′-bipyridyl	Extra pure	E.Merck
21.	1,10-Phenanthroline (Monohydrate)	G.R.	E.Merck
22.	Toluene	A.R.	E.Merck
23.	Xylene	Extra pure	E.Merck
24.	Cyclohexanone	G.R.	E.Merck
25.	Chloroform ($CHCl_3$)	G.R.	E.Merck
26.	Carbon tetrachloride	A.R.	E.Merck
27.	Kerosene	-	Locally supplied
28.	Hydrochloric acid	A.R.	E.Merck
29.	Methanol	A.R.	E.Merck

2.2 EQUIPMENTS

2.2.1 pH-meter

The pH measurements of metal ion solutions and of aqueous phase before equilibration were carried out on a combined electrode pH-meter (Toshniwal) at room temperature(25 ± 1°C). These pH measurements were carried out after due standardisation of pH-meter using 0.05M potassium hydrogen phthalate (pH 4.05) and 0.05M borax (pH 9.18) buffers.

2.2.2 Atomic absorption spectrophotometer

The concentration of the metal ions before and after each equilibration was determined on a Perkin-Elmer atomic absorption spectrophotometer model 3100 in which automatic curve corrections are made for incorporation of microprocessor. Thus, by using absorption data from linear and non-linear curves this instrument calibrates and computes concentration of its own.

2.2.3 UV-Vis spectrophotometer

Beckman DU-6 spectrophotometer, which is microprocessor controlled computing spectrophotometer operating in Ultra-Violet and Visible regions of the electromagnetic spectrum in the range 190-325 nm using Deuterium source and 325-900 nm using Tungsten source, respectively, has been employed for recording electronic spectra of the metal ion and ligand solutions and the blue coloured complex, for spectrophotometric determination of metal ions, for determining stability constant and complex composition, for analyzing effect of different metal ions in the range of 325-700 nm in water. Hence, its use to a general-purpose spectrophotometer for analytical and investigative purpose has been extended.

2.2.4 Infrared spectrophotometer

Fourier transform infrared (FTIR)-1600 instrument was used for recording IR spectrum of the Schiff base synthesized in the range of 4000-600 cm^{-1} in KBr.

2.3 METHODOLOGY

2.3.1 Spectrophotometric determination of Cu(II) using 3-Amino-5-mercapto-1,2,4-triazole

Stock metal ion solution (1.0×10^{-2}M) and an extractant solution (5.0×10^{-2}M) were prepared by dissolving the required amount of $CuCl_2.2H_2O$ and 3-Amino-5-mercapto-1,2,4-triazole in distilled water. The electronic spectra of metal ion and extractant solutions were scanned by DU-6 spectrophotometer in the range 325-700 nm with reference to water. Spectra of complex formed by taking equal volumes (5.0ml)of metal ion solution and extractant was scanned in the same wavelength region with reference to extractant (5.0×10^{-2}).

After interpreting the electronic spectra of complex, λ_{max} i.e. the wavelength at which maximum absorbance was observed, was obtained and the calibration plot was obtained for 0.05 - 0.50×10^{-3}M concentration of metal ion solution at λ_{max} 336 nm and 515 nm and for 0.08×10^{-3}M - 5.0×10^{-3} M concentration of metal ion solution at λ_{max} 348 nm and 512 nm with constant ligand concentration (25.0×10^{-3}M) in solution

2.3.2 Determination of the stability constant and composition of complex formed in aqueous media

2.3.2.1 Job's method

Stability constant and composition was determined by Job's continuous variation method.

Stock solution of metal ion (1.0×10^{-2}M) and of ligand (1.0×10^{-2}M) were prepared by dissolving an appropriate amount of them in distilled water.

Absorbance at λ_{max} 336 nm was obtained for different solutions of metal and ligand concentration which increases for one with corresponding decrease in concentration of other so as to keep the total concentration of solution at a constant value of 1.0 x 10^{-2}M. Plot was obtained between mole fraction of ligand vs. absorbance and calculations were done.

2.3.2.2 Molar ratio method

Composition of the complex formed was determined and hence confirmed by Molar ratio method in which the concentration of metal ion in the solution was kept constant by taking 5.0 ml of 1.0x10^{-2}M $CuCl_2.2H_2O$ solution in each observation and the concentration of the ligand correspondingly in each such observation was varied by taking different volumes of ligand (in ml) of 1.0x10^{-2}M concentration. Total volume was kept at 15 ml by compensating it through water. Composition was found out by the extrapolation of the graph plotted between volume of ligand taken vs. the corresponding absorbances.

2.3.3 Extraction of Cu(II) using triazole as an extractant in different diluents at different pH

Stock solutions of metal ion (1.0x10^{-2}M) and extractant (5.0x10^{-2}M) were prepared as mentioned previously. The concentration of the Cu (4.0 - 1.0 ppm) in the diluted samples were determined on the Perkin Elmer atomic absorption spectrophotometer and instrument was calibrated for each set of readings.

Equal volumes (15.0 ml) of aqueous phase consisting of 5.0 ml of metal ion (1.0x10^{-2}M) and 5.0 ml of extractant (5.0x10^{-2}M) in 5.0 ml of the buffer solution of the desired pH and organic phase were shaken in a separating funnel at room temperature for 5-10 minutes to ensure complete equilibration. The concentration of metal ion[Cu (II)] in aqueous phase was determined by using atomic absorption spectrophotometer at 324.7 nm using an air-acetylene flame after the two phases were separated clearly.

Five sets of experiments have been done for triazole with Cu(II) ion solution.

For the first set of experiment, the metal ion concentration (1.0×10^{-2}M) and the triazole concentration (5.0×10^{-2}M) were kept constant and the extractions were carried out as a function of pH using KH_2PO_4-NaOH (4.0 - 8.4) and CH_3COOH-CH_3COONa (4.25 - 5.50) buffers.

Extraction studies in conjugation with atomic absorption spectrophotometry were carried out in different solvents, the choice of which was done on the basis of properties such as selectivity, distribution coefficient, capacity, solubility, density, recoverability, chemical reactivity and stability, viscosity, etc. [4]. Studies have been carried out in different pH ranges for each solvent. For different solvents varying shaking time was required to get equilibration.

Second set of experiments involved a constant [metal ion]=(1.0×10^{-2}M) and pH[(at which the maximum extraction of metal occurred (4.25 - 5.50)] and extractions were carried out as a function of concentration of extractant (0.25×10^{-3}M-25.0×10^{-3}M) with only one diluent.

In the third set of experiments, concentration of the extractant (5.0×10^{-2}M) and pH [at which maximum extraction of metal occurred (4.25-5.50)] were kept constant and extractions were done as a function of concentration of metal ion (0.1×10^{-3}M - 5.0×10^{-3}M). In both the sets the concentration of metal ion was determined by atomic absorption spectrophotometer and DU-6 spectrophotometer.

In the fourth set of observations, extraction behaviour in various diluents(toluene, xylene, chloroform, carbon tetrachloride, kerosene and cyclohexanone) was studied at constant [metal ion], [extractant], pH and shaking time.

Last set of experiments included the study of the effect of metal ions [eg. Fe(III)] in the determination of Cu(II) by atomic absorption spectrophotometry at 248.3nm using an air-acetylene flame and a number of metal ions (using 300-fold excess) by DU-6 spectrophotometer.

Absorbance was measured at λ_{max} 348 and 512 nm vs. a solution containing 5.0 ml each of 1.0×10^{-2}M Cu (II) solution, 5.0×10^{-2}M of triazole and distilled water.

The distribution ratio (D) and the percentage extraction (%E) were calculated using the following relations:

$$D = \frac{\text{Concentration of metal ion in organic phase}}{\text{Concentration of metal ion in aqueous phase}} \qquad (7)$$

$$\%E = \frac{\text{Concentration of metal ion in organic phase}}{\text{Total concentration of metal ion}} \times 100 \qquad (8)$$

Concentration of metal ion in organic phase was calculated by difference of original metal ion concentration in aqueous phase before and after equilibration.

For all sets of experiment % E, D and log D values were calculated, the results are given in next chapter.

2.3.4 Back extraction

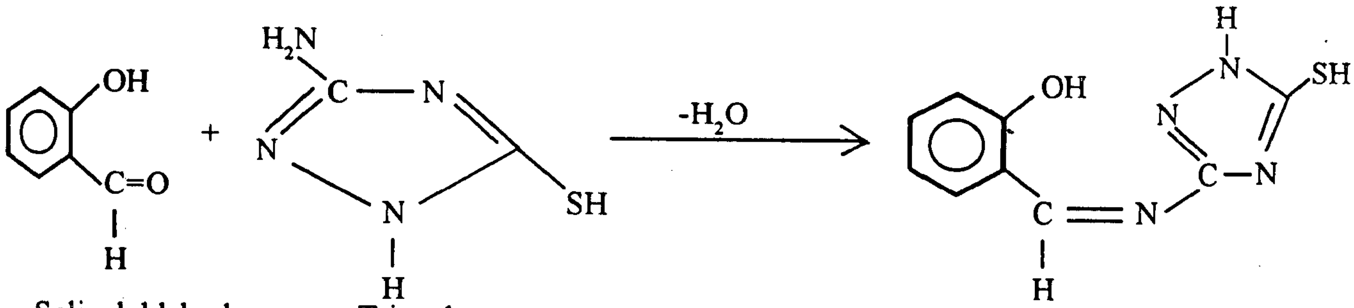
The recovery or back extraction of metal ion which was transferred into the organic phase (toluene) was done by using HCl solutions of different molarity (1.0M-3.0M) .

Equal volumes (15.0ml) of organic phase [left after equilibration with aqueous phase] containing metal ions and aqueous phase (15.0ml) containing HCl (1.0M-3.0M) were shaken for 25-30 minutes to ensure complete equilibration. After clear separation of the two phases, the concentration of metal ion in aqueous phase was determined by using atomic absorption spectrophotometer.Then %E, D and $\log_{10}$ D were calculated and plotted . Here, extraction was carried out as a function of acid molarity.

2.3.5 Extraction of Cu(II) using Schiff base derived from the condensation of salicylaldehyde and 3-Amino-5-mercapto-1,2,4-Triazole

2.3.5.1 Synthesis

The schiff base was synthesized by refluxing equimolar amounts of salicylaldehyde and 3-amino-5-mercapto triazole according to the following equation:



Salicylaldehyde (Mol wt. = 122.12 g)
Triazole (Mol wt. = 116.12 g)
Schiff base (220.24 g)

Triazole (1.9022g, 0.0164mole) was dissolved in 35-40ml of water at 50-60^{0}C temperature with constant stirring for 1 hr. To this was added 1.72ml(2.0003g/0.0164 mole) of salicylaldehyde in 5.0-10.0ml of methanol and again the resulting mixture was stirred for 1-2 hr and then refluxed for 4-5 hrs. A yellow solution was subjected to steam distillation in order to remove excess of the solvent. The dirty white solid was obtained on cooling which was dried, weighed. Infrared spectrum of the solid was recorded [ν (C=N), **1640cm^{-1}**(s); ν (S-H),**2606**cm^{-1}(w);ν(O-H),**3100-3300**cm^{-1}(s)].

Colour : Dirty white

% Yield : 72.3%

Melting point :250 - 255^{0}C^d

2.3.5.2 Extraction of Cu(II) using Schiff base as an extractant at varying pH

Equal volume (15.0 ml) of aqueous phase containing 5.0 ml of metal ion solution (1.0×10^{-2}M) and 5.0 ml of Schiff base (5.40×10^{-2}M) in 5.0 ml of the buffer solution of the desired pH and organic phase (kerosene as diluent) were shaken for 20-25 min in order to achieve equilibration. After the two phases were separated clearly, the concentration of metal ion in aqueous phase was determined by atomic absorption spectrophotometer at 324.7 nm. %E, D and $\log_{10}$ D were calculated and plotted.

2.3.5.3 Back extraction

The metal ion transferred to the organic phase after extraction using Schiff base as an extractant was recovered by shaking equal volume (15.0 ml) of organic phase (obtained on separating aqueous layer after previous extraction) and 4.0M-HCl in aqueous phase. After shaking for 20-25 min, the concentration of aqueous phase was determined by using atomic absorption spectrophotometer, as soon as the separation becomes clear. The results are given and discussed in the next chapter.

2.3.6 Synergistic extraction of Cu(II) with triazole using 2,2′-bipyridine and 1,10-phenanthroline

Synergistic effect of 2,2′-bipyridine and 1,10-phenanthroline was studied for the extraction of Cu(II) into different diluents at constant pH. Stock solutions of metal ion (1.0×10^{-2}M), extractant (5.0×10^{-2}M), 2,2′-bipyridine (5.0×10^{-2}M) and 1,10,-phenanthroline (5.0×10^{-2}M) were prepared in distilled water.

Equal volumes (20.0 ml) of aqueous phase consisting 5.0 ml each of Cu(II) ion (1.0×10^{-2}M), triazole (5.0×10^{-2}M), 2,2′-bipyridyl (5.0×10^{-2}M) or 1,10, phenanthroline (5.0×10^{-2}M) and organic phase were shaken for 20-25 min. till the equilibration was achieved. After that the two layers were allowed to settle to bring about clear separation and then the concentration of metal ion in aqueous phase was determined by atomic absorption spectrophotometer and %E, D, Log_{10} D are calculated for different diluents viz. kerosene, toluene, xylene, carbon tetrachloride and chloroform.

RESULTS & DISCUSSION

3.1 Spectrophotometric determination of Cu(II) using 3-Amino-5-mercapto-1,2,4-triazole

Results obtained for the spectrophotometric determination of Cu(II) using triazole can be summarized as follows:

3.1.1 Electronic spectrum to find λ_{max}

Electronic spectra of the Cu(II) solution (1.0×10^{-2}M) Cu(II) and triazole solution (5.0×10^{-2}M) in water was recorded in the range 250.0 nm - 700.0 nm with reference to water (Fig. 2). Also, spectrum of the complex [5.0 ml of (1.0×10^{-2}M) Cu(II) and 5.0 ml of (5.0×10^{-2}M) triazole in water] was recorded in the range 325.0 nm - 700.0 nm with reference to triazole (5.0 ml of triazole + 5.0 ml of water] as well as with reference to water and four peaks were found at 336.0 nm, 348.0 nm, 512.0 nm and 595.0 nm [Fig.3]. Rest of the spectrophotometric studies were carried out at 336·0, 348·0 & 512.0 nm because at these wave lengths Cu(II) and triazole solutions are absorbed in very small amount.

3.1.2 Verification of Beer's law and spectrophotometric determination of Cu(II)

The absorbances recorded for 0.08×10^{-3}M - 5.0×10^{-3}M of Cu(II) ion at λ_{max} 348.0 nm and 512.0 nm are tabulated in Table 2. Plot of absorbances vs. respective concentrations of metal ion is shown in (Fig. 4) which is observed to be linear within the concentration range 0.0 - 3.0×10^{-3}M of Cu(II) at 348.0 nm and 512.0 nm.

Similarly, absorbances obtained for 0.02×10^{-3}M - 0.5×10^{-3}M of Cu(II) at λ_{max} 336.0 nm are tabulated in Table 3 and the corresponding plot is shown in

(Fig. 5) which is observed to be linear within the given concentration range.

Hence, Beer's law was obeyed in the concentration range 0.0 - 3.0×10^{-3}M [0.0-129.0 ppm] Cu(II) ion in solution. Further, absorbances of three unknown samples at these wavelengths (λ_{max}) were recorded and concentration of Cu(II) was calculated from the calibration plots and the results are given below. The results indicated that Cu(II) was spectrophotometrically determined quantitatively in aqueous phase using triazole (Tabulated in Table 4).

The molar absorptivity (ϵ) was 9.90×10^{3} $\mathrm{Lmol^{-1}cm^{-1}}$ at λ_{max} 336.0 nm and 1.36×10^{3} L $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$ at λ_{max}. 512.0 nm.

3.1.3 Composition and Stability constant of the complex

The composition and stability constant of the blue coloured complex formed was determined by Job's continuous variation method. Here, the concentration of Cu(II) and triazole (both have initial concentration 1.0×10^{-2}M) were varied keeping the total volume constant. The absorbance was recorded at λ_{max} 336.0 nm which are tabulated in Table 5 at constant pH 2.50 and the plot of the absorbance against the mole fraction of ligand is shown in Fig. 6. The following equations were used to calculate stability constant and composition of the complex :

$$K = \frac{(A/A_{exp}) \times C}{\left(C_m - \frac{A}{A_{exp}} \times C\right)\left(C_L - \frac{A}{A_{exp}} \times C\right)} \qquad (9)$$

where, k is stability constant

C is total concentration

C_m is concentration of metal

C_L is concentration of ligand

C is point A′ in the graph

$$n = \frac{m.f.}{1 - m.f.} \qquad (10)$$

where, m.f. is mole fraction of ligand used for complex formation

n is number of ligand molecules in the complex.

From the calculations, stability constant was 1.80 and n was 1.38, thus suggesting that most probably Cu(II) forms 1:2 complex with the triazole [Cu(II) : triazole].

The composition of Cu(II): triazole (1:2) was also confirmed by molar ratio method. In this method, volume of 1.0×10^{-2}M Cu(II) was kept constant and volume of 1.0×10^{-2}M triazole was varied continuously. Absorbances were measured at λ_{max} 348.0 nm which are tabulated in Table 6. A graph was plotted between absorbance and volume of ligand (ml) (Fig. 7). Graph was extrapolated to meet at a point from where when a line was drawn perpendicular to x-axis gives the volume of ligand relative to 5.0 ml of Cu(II). This gives the metal to ligand ratio to be 1:1.48. Hence, formation of 1:2 complex between Cu(II) and triazole is confirmed.

3.2 Solvent extraction studies of Cu(II) with triazole

Extraction of Cu(II) from the aqueous medium into organic solvent using triazole as an extractant proves to be a good example of solution chemistry as effect of pH and the reaction occurring in solution provides an opportunity in formulation of the basis of the studied extracting system. We can divide the results obtained on studying various parameters into following groups :

3.2.1 Effect of pH of aqueous phase

The pH of 10.0 ml of aqueous solution containing 5.0 ml of 1.0×10^{-2}M Cu(II) solution and 5.0 ml of 5.0×10^{-2}M triazole was found to be 2.50 ± 0.2. It was found that at this pH there was no phase transfer of Cu(II) complex from aqueous phase to organic phase because the solution is highly acidic and the equilibrium existing between free metal ion and triazole and the complex is greatly shifted to the left, i.e.

$$M^{2+} + L_n\text{-}mH \rightleftharpoons M\text{-}L_n + mH^+ \qquad (11)$$

as there are no other species present which can remove H^+ from solution. Hence, at low pH no extraction occurs. *Further, neutral molecule is the essential requirement for extraction into organic phase and at low pH the complex was highly ionic species.* So, it was formulated that increase in pH makes the complex neutral and this was achieved by using two buffers: one, CH_3COOH-CH_3COONa of the pH range 4.30 - 5.60 and another KH_2PO_4 - NaOH of the pH range 5.60 - 8.80.

It was found that with the increase in pH the percent extraction increased and hence distribution coefficient (D) was also increased, but as soon as we go to higher pH range>5.60, the precipitate formed, which was probably due to the precipitation of some Cu(II) salt and hence KH_2PO_4 - NaOH buffer was discarded on this ground and further studies were concentrated on acetate buffer in the pH range 4.30 - 5.60. For this buffer, the percent extraction increases with increase in the pH of the aqueous phase, reaches a maximum value upto pH 5.30 and thereafter it decreases.

Extraction studies as a function of pH were carried out for six solvents viz., toluene, xylene, cyclohexanone, carbon tetrachloride, chloroform and kerosene. The percent extraction for each of these solvents as a function of pH is tabulated in Table 7 and the percent extraction was plotted versus pH as shown in Fig.8. From these results it was formulated that 5.28 is the pH for optimum extraction and kerosene is the best extracting solvent among the studied solvents, simply because less time is required for equilibration (Table 8), the maximum extraction takes place and the organic phase does not have any suspended particles as was observed in the case of other solvents. In case of toluene also, no suspended particles were present after extraction. On the basis of these results, extraction of Cu(II) from a solution containing constant metal ion (1.0×10^{-2}M) and triazole (5.0×10^{-2}M) concentration into kerosene and toluene as a fucntion of pH (4.29 - 5.50) was further carried out and results are tabulated in Tables 9 and 10. Plot of $\mathrm{Log}_{10}(D)$ with respect to pH is shown in (Fig. 9). It was found that plot for toluene has slope 0.467 which suggests two things:

1) that distribution of distribution constant is normal and various values are lying around the distribution curve and
2) that percent extraction and hence distribution coefficient varies in small intervals with the increase in pH of the aqueous phase.

On the other hand slope of 0.70 for kerosene as solvent suggests that there is sharp and sudden increase in percent extraction and that points are lying close to the distribution curve. The plot also suggests that the extraction increases with increase in pH and extraction studies can only be carried out between pH 4.50-5.50 because below pH 4.50 solution is acidic enough to shift the equilibrium (Equation 11) towards left. Hence the H^+ are formed during the formation of the complex species that can be extracted into organic phase.

3.2.2 Effect of metal ion concentration

The effect of Cu(II) ion concentration within the range ($0.1x10^{-3}$M-$5.0x10^{-3}$M) on the distribution ratio was studied at constant ligand concentration ($5.0x10^{-2}$M) and constant pH (at which maximum extraction occurred) using kerosene as a solvent. The results are tabulated in table 11. A plot of percent extraction with respect to metal ion concentration (Fig. 10) was approximately a straight line, which suggests that extraction was independent of metal ion concentration in the above range indicating that the same species extracts in the cited concentration range. The plot of $\log_{10}$(D) with respect to metal ion concentration (Fig. 10) has slope 0.1875 which suggests that the distribution curve was not normal with respect to extraction at various Cu(II) concentration.

3.2.3 Effect of extractant concentration

The extent of extraction of Cu(II) with varying concentration of extractant ($0.5x10^{-3}$M - $25x10^{-3}$M) at constant metal ion concentration ($1.0x10^{-2}$M) and pH (at which maximum extraction occurred) of the aqueous phase was investigated and the percent extraction over the cited range is tabulated in Table 12. The plot of percent extraction and $\log_{10}$(D) versus $\log_{10}$(ligand) (fig. 11) seems to be linear as graph comes out to be straight line. Slope was found to be 0.545. At very high concentration of ligand $>20x10^{-3}$M the graph deviates from linearity.

The straight line doesn't confirms the extraction by the formation of 1:2 complex.

It has been observed that for ligand concentration $<5.0 \times 10^{-3}$M unstable complexes were formed, colour of which changes from blue to black as soon as buffer is added.

Hence, from the above discussion it is interpreted that for maximum extraction of Cu(II) in the range (0.1×10^{-3}M-5.0×10^{-3}M) the triazole of (5.0×10^{-3}M - 20×10^{-3}M) concentration should be required at pH 5.30 ± 0.10 taking kerosene and toluene as extracting solvents .

3.2.4 Effect of interferring metal ion

Extraction studies of the solution containing 5.0 ml of (1.0×10^{-2}M) Fe(III) ions in 5.0 ml of (1.0×10^{-2}M) Cu(II) ion, 5.0 ml of (5.0×10^{-2}M) triazole and 5.0 ml of buffer of appropriate pH of the aqueous phase were carried out as a function of pH into kerosene as a diluent. The absorbance and corresponding concentration was measured using a Perkin Elmer atomic absorption spectrophotometer in an air-acetylene flame and at 248.3 nm for Fe and 324.7 nm for Cu. The percent extraction, corresponding D values and $\log_{10}(D)$ values are tabulated in Table 13. A graph between $\log_{10}(D)$ versus pH was plotted (Fig. 12). The two plots suggests that the slope for distribution curve of Cu(II) is more than that of Fe(III) which confirms that percent extraction of Cu(II) increases as pH increases while that of Fe(III) remains constant over the entire pH range. Fe(III) interferred seriously in the extraction of Cu(II). Fe(III) also gets extracted in the range of 65.0-70.0 %. Hence, extraction of Cu(II) can be carried out selectively in presence of Fe(III) by masking the later ion and carrying out the extraction at pH 5.50.

3.3. Back extraction

Recovery of Cu(II) extracted into the organic phase by extracting back into the aqueous phase can be achieved by using a highly acidic (HCl) aqueous solution because the complex in the neutral form is transferred into the organic phase (a phase which is less ionic than the aqueous phase) and its stability in the organic phase can only be diminished by increasing the H^+ ion concentration so that more hydrogen ions are available for coordination with ligand which in turn loose coordination with Cu(II), thus facilitating the phase transition of Cu(II) from the organic phase to the aqueous phase.

In the present study HCl solution was used to extract back Cu(II) from toluene as an organic phase for the constant initial metal ion (1.0×10^{-2}M) concentration and ligand (5.0×10^{-2}M) concentration. Back extraction was carried out by using 1.0-,2.0M- and 3.0M-HCl solution of pH 1.23±0.02, 1.12±0.02 and 0.93±0.02, respectively. At lower pH of HCl used, higher will be the affinity of aqueous medium for Cu(II) ions formed by dissociation of Cu(II)-triazole complex according to equilibria

$$\underset{\text{Complex}}{ML_n(org)} + nH^+ \rightleftarrows M^{2+} + L_n - nH \qquad (12)$$

The percent extraction (back) from the organic to the aqueous phase was investigated as a function of pH for different molarities of HCl solution. The results obtained are tabulated in the Tables 14-16. The plot of $\log_{10}D$ versus pH (Fig. 13) shows straight line for all the acid molarities investigated.

Results obtained with 3.0M-HCl are best distributed with pH at which the extraction to the organic phase occurred as slope of the curve is 1.60 which suggests that with the increase in pH percent of back extraction increases and maximum extraction can be achieved at pH 5.50. For 2.0M-HCl percent extraction remains constant over the pH range investigated with slope only 0.08 which suggests that at this acid molarity the number of hydrogen ion released over entire pH range coordinates back to ligand with almost same concentration. For 1.0M-HCl slope was 1.36, maximum back extraction was also achieved at pH 5.50 at which the extraction to the organic phase occurred but still this acidity is not high enough to dissociate Cu(II)-ligand bond.

Hence, back extraction can be achieved with good accuracy by increasing the molarity of HCl solution at pH 5.50 (Fig. 13).

3.4 Synergistic Extraction

Synergists are the species which enhance the extraction of metal ion into the organic phase. The synergistic effect of two extractants, 2,2'-bipyridine and 1,10-phenanthroline, was investigated for a constant Cu(II) ion (1.0×10^{-2}M) concentration and ligand (5.0×10^{-2}M) concentration into different diluents. The percent extraction at constant pH 5.90 for various diluents is tabulated in Table 17.

This effect was investigated because the blue coloured complex which was transferred from the aqueous phase to the organic phase was not completely soluble, rather it appeared to be in suspended form. So to test whether these synergists transfer the complex to organic phase to form a clear solution was investigated and the percent extraction was found for different solvents. Results shows a decrease in percent extraction at this pH (5.90) and it decreases as the pH of the solution decreases. Thus, it is concluded that the cited extractants have no synergistic effect rather it *destabilizes the complex in the organic phase which leads to decreased* $\log_{10}(D)$ *values.* Also, the stability of the complex MR_nS_x formed according to the reaction

$$M^{n+} + nHR + xS \longrightarrow MR_nS_x + nH^+ \qquad (13)$$

is questionable, as had the complex of such composition formed the percent extraction would have been increased. *Further, the 6-coordinated octahedral Cu(II) complex, of the type* $[Cu(L)L'_2]$ *(where L = 2,2'-bipyridyl or 1,10-phenanthroline L' = an ion of triazole) may not be very stable in comparison to the square planar complex of Cu(II) with triazole* (CuL'_2).

3.5 Extraction of Cu(II) using Schiff base

3.5.1 Infra red spectrum of Schiff base

IR spectrum of the Schiff base in the range 4000 cm^{-1} to 666 cm^{-1} was recorded and the stretching frequency of the azomethine group(>C=N-) group has been assigned at 1640 cm^{-1} (Fig. 14).

3.5.2 Extracton with 5.4×10^{-2}M Schiff base

Extraction of Cu(II) (1.0×10^{-2}M) with (5.4×10^{-2}M) Schiff base was investigated as a function of pH into kerosene. The percent extraction and $\log_{10}D$ has been tabulated in Table 18. A plot of $\log_{10}(D)$ versus pH comes to be a straight line with slope 2.20 (Fig. 15), which suggests that percent extraction and hence distribution coefficient is a function of pH and it increases if pH increases and decreases if pH decreases. Also, the optimum pH for the extraction was 5.50. The increased percent of extraction is attributed to the fact that the Schiff base possesses greater efficiency than triazole to coordinate with Cu(II) and thus neutralizing it for transfer into organic phase because of the presence of a mercapto group and an alcoholic group which provides extra stability because of the ability to form hydrogen bonding. *The*

Schiff base acts as a tridentate dibasic and fourth cordinating position around Cu(II) may be occupied by water molecule.

3.5.3 Back extraction from organic phase

Recovery of Cu(II) from the organic phase back into the aqueous phase consisting of 4.0M-HCl at constant initial metal ion concentration (1.0×10^{-2}M) and ligand concentration (5.4×10^{-2}M) was investigated and percent back extraction from the organic phase as a fucntion of pH, at which the extraction to the organic phase occurred, is tabulated in Table 19. A graph has been plotted between $\log_{10}(D)$ versus pH (Fig. 15) and its slope comes out to be -0.56 which suggests that with the increase in pH the percent back extraction decreases. This decrease in percent back extraction from the organic to the aqueous phase is attributed to the fact that *Schiff base formed a stable complex (higher than the stability of triazole complex) with Cu(II) in the organic phase which is difficult to dissociate in the studied pH range.*

Hence, Schiff base can be used for the extraction of Cu(II) into the organic phase but the back extracton into the aqueous phase is difficult.

3.6 Spectrophotometric investigation of interfer-ence due to various ions

The investigation of interferrence caused by various ions was carried out using DU-6 spectrophotometer. Absorbance was measured at 348.0 nm and 512.0 nm for solution containing 5.0 ml each of (1.0×10^{-2}M) Cu(II), (5.0×10^{-2}M) triazole and either 0.05, 0.1, 0.25, 0.5 or 1.0M of interfer-ing salt in solution and the results are tabulated in Table 20. It was assumed that the concentration of intefer-ing ion in solution was either 15-, 30-, 150- or 300- fold to that of Cu(II) (3.3×10^{-3}M) concentration in solution depending upon the solubility of a particular salt in water. Reference was taken as 5.0 ml each of (1.0×10^{-2}M) Cu(II) ion solution and (5.0×10^{-2}M) ligand solution in 5.0 ml of water. The absorbances measured were compared with the calibration plot of Cu(II) solution at the above mentioned wavelengths obtained in fig.4.

To study the interference effect we can divide our observations into the following two groups:

i) For concentration of salts 0.5M or 1.0M in solution i.e., 150 or 300 times to the metal ion concentration [Cu(II)] in solution:

At 348.0 nm all the ions interfered as the absorbances of the complex was far below than they would be expected at 3.3×10^{-3}M solution concentration of Cu(II) ions.

At 512.0 nm Ag(I), Co(II) and Zn(II) ions absorb greatly and shows peak in their spectrum alongwith their λ_{max} at 429.0 nm, 522.0 nm and 423.0 nm, respectively. Other ions viz. Ba(II), Ni(II), Pb(II), Na^+, K^+ absorb very less at this λ_{max} (512.0 nm), Ni(II) shows its absorption peak at 400.0 nm (green coloured solution).

ii) For concentration of salts 0.05M or 0.1M in solution i.e., 15 or 30 times to the metal ion concentration [Cu(II)] in solution:

At 348.0 nm all the salts absorb weakly relative to the absorbance of Cu(II) (1.48 for 3.3×10^{-3}M Cu(II) in solution) and hence cause little interference.

At 512.0 nm Ba(II), Zn(II), Ni(II), Pb(II), K^+, Na^+ absorb weakly relative to 0.82 absorbance for 3.3×10^{-3}M of Cu(II) in solution and cause little interference. On the other hand, Ag(I) and Fe(II) absorb heavily thus causing interference in the determination of Cu(II) with the absorption maxima in their spectrum at 423.0 nm and 383.0 nm, respectively. Co(II) causes small interference as it absorbs slightly less (0.733) than Cu(II) (0.820). Ni(II), Pb(II), Na^+ shows absorption maxima in their spectrum at 392.0, 366.0 and 359.0 nm, respectively.

Hence, it can be concluded that Ag(I) and Fe(II) interfere at low concentrations also when they are present in solution alongwith Cu(II), and Co(II), Zn(II) and Ag(I) interfere at high concentrations when present with Cu(II).

TABLE 2

Measurement of absorbance with concentration of Cu(II) ion in solution (0.08×10^{-3} M- 5.0×10^{-3} M) taking 25×10^{-3} M concentration of Ligand (5.0×10^{-2}M) in solution

S.No.	Concentration of metal ion (1.0×10^{-2}M) in solution	Concentration of triazole (5.0×10^{-2}M) in solution	Absorbance at λ_{max}	
			348.0 nm	512.0 nm
1.	0.08×10^{-3}M	25×10^{-3} M	0.11	0.00
2.	0.10×10^{-3}M	25×10^{-3} M	0.15	0.01
3.	0.50×10^{-3}M	25×10^{-3} M	0.34	0.08
4.	0.80×10^{-3}M	25×10^{-3} M	0.46	0.14
5.	1.00×10^{-3}M	25×10^{-3} M	0.56	0.19
6.	2.00×10^{-3}M	25×10^{-3} M	0.98	0.45
7.	3.00×10^{-3}M	25×10^{-3} M	1.42	0.73
8.	4.00×10^{-3}M	25×10^{-3} M	1.85	1.04
9.	5.00×10^{-3}M	25×10^{-3} M	2.23	1.31

TABLE 3

Measurement of absorbance with concentration of Cu(II) ion in solution (0.02×10^{-3}M - 0.5×10^{-3}M) taking 2.5×10^{-3} M concentration of Ligand (5.0×10^{-2}m) in solution

S.No.	Concentration of metal ion (1.0×10^{-2}M) in solution	Concentration of triazole (5.0×10^{-2}M) in solution	Absorbanc at λ_{max} 336.0 nm
1.	0.02×10^{-3}M	2.5×10^{-3}M	0.04
2.	0.04×10^{-3}M	2.5×10^{-3}M	0.06
3.	0.06×10^{-3}M	2.5×10^{-3}M	0.11
4.	0.08×10^{-3}M	2.5×10^{-3}M	0.095
5.	0.10×10^{-3}M	2.5×10^{-3}M	0.16
6.	0.50×10^{-3}M	2.5×10^{-3}M	0.89

TABLE 4

S. No.	Calculated Concentration	Observed Absorbance	Observed Concentration
1.	0.85×10^{-3}M	0.423 (λ_{max}348.0nm)	0.9×10^{-3}M
2.	1.25×10^{-3}M	0.594 (λ_{max}348.0nm)	1.25×10^{-3}M
3.	0.50×10^{-3}M	0.201 (λ_{max}348.0nm)	0.45×10^{-3}M

TABLE 5

Data for calculation of stability constant and composition of the complex by Job's continuous variation method

S.No.	Volume of 1.0×10^{-2}M Cu(II) solution (ml)	Volume of 1.0×10^{-2}M Triazole solution (ml)	Concentration of Triazole (C_L)	Mole fraction (C_L/c)	Absorbance at λ_{max} 336.0 nm
1.	1.0	9.0	0.9×10^{-2} M	0.9	0.72
2.	2.0	8.0	0.8×10^{-2} M	0.8	1.26
3.	3.0	7.0	0.7×10^{-2} M	0.7	1.80
4.	4.0	6.0	0.6×10^{-2} M	0.6	2.16
5.	5.0	5.0	0.5×10^{-2} M	0.5	2.03
6.	6.0	4.0	0.4×10^{-2} M	0.4	1.73
7.	7.0	3.0	0.3×10^{-2} M	0.3	1.32
8.	8.0	2.0	0.2×10^{-2} M	0.2	0.89
9.	9.0	1.0	0.1×10^{-2} M	0.1	0.50
10.	10.0	0.0	0.0×10^{-2} M	0.0	0.00

TABLE 6

Data for Molar ratio method for the determination of stability constant and composition of the complex

S.No.	Volume of 1.0×10^{-2}M Cu(II) solution V_M(ml)	Volume of 1.0×10^{-2}M Triazole V_L(ml)	Volume of water (ml)	Absorbance at λ_{max} 348.0 nm
1.	5.0	1.0	9.0	0.19
2.	5.0	2.0	8.0	0.35
3.	5.0	3.0	7.0	0.50
4.	5.0	4.0	6.0	0.666
5.	5.0	5.0	5.0	0.85
6.	5.0	6.0	4.0	1.01
7.	5.0	7.0	3.0	1.19
8.	5.0	8.0	2.0	1.26
9.	5.0	9.0	1.0	1.41

TABLE 7

Extraction of 1.0 x 10^{-2}M Cu(II) with 5.0 x 10^{-2}M Triazole as a function of pH of the aqueous phase with different extracting solvents

S.No.	pH	% Extraction					
		Toluene	Xylene	Cyclo-Hexanone	Chloroform	Carbon Tetrachloride	Kerosene
1.	4.74	98.82	97.94	90.79	99.62	99.01	99.32
2.	4.88	99.52	98.32	94.07	99.77	95.06	99.55
3.	5.12	99.25	99.55	90.34	95.70	99.06	99.86
4.	5.28	99.35	99.49	91.26	98.71	99.73	99.59
5.	5.50	99.16	99.05	92.78	98.61	99.38	99.85

TABLE 8

Extraction of 1.0 x 10^{-2}M Cu(II) with 5.0 x 10^{-2}M Triazole at constant shaking time with different extracting solvents at pH 4.74 and 5.28

S.No.	Solvent	Dielectric Constant[9]	Shaking time	% Extraction at pH=4.74	%Extraction at pH=5.28
1.	Toluene	2.38	25-30 min	98.82	99.35
2.	Xylene	2.37	25-30 min	97.94	99.49
3.	Cyclohexanone	18.20	30-35 min	90.79	91.26
4.	Chloroform	4.90	20-25 min	99.62	98.71
5.	Carbontetra-chloride	2.24	20-25 min	99.01	99.73
6.	Kerosene	-	05-10 min	99.32	99.59

TABLE 9

Extraction of 1.0 x 10^{-2}M Cu(II) with 5.0 x 10^{-2}M Triazole as a function of pH using kerosene as an extracting solvent

S.No.	pH	% Extraction	Distribution coefficient, D	$\log_{10} D$
1.	4.29	93.36	14.0730	1.1484
2.	4.50	99.28	139.5383	2.1447
3.	4.74	99.32	146.2574	2.1651
4.	4.88	99.55	221.8608	2.3461
5.	5.12	99.86	732.1933	2.8646
6.	5.28	99.59	241.6982	2.3833
7.	5.50	99.86	711.2449	2.8520

TABLE 10

Extraction of 1.0 x 10^{-2}M Cu(II) with 5.0 x 10^{-2}M Triazole as a function of pH using Toluene as an extracting solvent

S.No.	pH	% Extraction	Distribution coefficient, D	$\log_{10} D$
1.	4.29	92.63	12.5728	1.0994
2.	4.50	99.24	130.7654	2.1165
3.	4.74	98.82	83.7877	1.9232
4.	4.88	99.52	210.4706	2.3232
5.	5.12	99.25	131.7384	2.1197
6.	5.28	99.35	153.0714	2.1849
7.	5.50	99.16	118.5014	2.0737

TABLE 11

Extraction of Cu(II) with 5.0 x 10^{-2}M Triazole at a constant pH 5.37, as a function of metal ion concentration using kerosene as an extracting solvent

S. No.	Concentration of metal ion in solution	Concentration of metal in aqueous phase after extraction (ppm)	% Extraction	Distribution coefficient, D	Log$_{10}$D
1.	0.1×10^{-3}M	0.553	87.41	6.9421	0.8415
2.	0.5×10^{-3}M	0.171	99.22	127.4210	2.1052
3.	1.0×10^{-3}M	0.192	99.56	227.7500	2.3574
4.	2.0×10^{-3}M	0.193	99.82	567.9119	2.7543
5.	3.0×10^{-3}M	0.441	99.73	372.4694	2.5711
6.	4.0×10^{-3}M	2.640	98.80	82.1818	1.9148
7.	5.0×10^{-3}M	1.646	99.40	165.7679	2.2195

TABLE 12

Extraction of Cu(II) at constant pH 5.37 and 1.0 x 10^{-2}M metal ion concentration, as a function of Triazole concentration using kerosene as an extracting solvent

S.No.	Concentration of Ligand (Triazole) L_n	Log L_n	% Extraction	Distribution coefficient, D	$Log_{10}D$
1.	0.5×10^{-3}M	-3.3010	99.10	110.7032	2.0441
2.	2.5×10^{-3}M	-2.6020	83.04	4.8976	0.6990
3.	5.0×10^{-3}M	-2.3010	99.57	229.6364	2.3610
4.	10×10^{-3}M	-2.0000	99.90	1047.0392	3.0199
5.	15×10^{-3}M	-1.8239	99.86	723.7457	2.8596
6.	20×10^{-3}M	-1.6990	99.79	466.8337	2.6691
7.	25×10^{-3}M	-1.6020	99.73	370.1805	2.5684

TABLE 13

Effect of interfering metal ion [Fe(III) $1.0x10^{-2}$M] for the extraction of Cu(II) $1.0x10^{-2}$M and ligand $5.0x10^{-2}$M as a function of pH into kerosene

S.No.	pH	% Extraction		Distributioncoeff.(D)		$\log_{10}$ D	
		Fe(II)	Cu(II)	Fe(II)	Cu(II)	Fe(II)	Cu(II)
1	4.29	67.72	83.15	2.0979	4.9333	0.3218	0.6931
2	4.50	68.18	96.90	2.1427	31.2914	0.3310	1.4954
3	4.74	68.46	99.14	2.1710	115.0481	0.3366	2.0609
4	4.88	66.94	99.77	2.0245	427.5185	0.3063	2.6310
5	5.12	67.07	99.71	2.0369	348.5468	0.3090	2.5423
6	5.28	67.44	99.80	2.0709	508.6916	0.3162	2.7064
7	5.50	68.87	99.93	2.2124	1376.3809	0.3449	3.1387

TALBE 14

Back extraction of metal ion from organic phase (Toluene) into 1.0 M-HCl containing aqueous phase

S.No.	pH at which extraction to the organic phase occurred	Concentration of organic phase (ppm)	Concentration of aqueous phase after back extraction (ppm)	Distribution coefficient,D	$\log_{10}$(D)
1.	4.29	172.22	1.12	0.006	-2.1840
2.	4.50	171.27	0.87	0.005	-2.2919
3.	4.74	172.10	0.00	0.000	0.000
4.	4.88	170.59	0.00	0.000	0.000
5.	5.12	170.05	0.00	0.000	0.000
6.	5.28	171.31	1.60	0.009	-2.0256
7.	5.50	170.59	37.00	0.2769	-0.5576

TALBE 15

Back extraction of metal ion from organic phase (Toluene) into 2.0M-HCl containing aqueous phase

S.No.	pH at which extraction to the organic phase occurred	concentration of organic phase (ppm)	concentration of aqueous phase after back extraction (ppm)	% Back extraction	Distribution coefficient, D	$Log_{10} D$
1.	4.29	168.24	32.431	19.27	0.2388	-0.6220
2.	4.50	169.20	35.625	21.05	0.2667	-0.5740
3.	4.74	169.84	37.596	22.14	0.2843	-0.5462
4.	4.88	170.00	38.621	22.72	0.2940	-0.5317
5.	5.12	170.38	39.784	23.35	0.3046	-0.5162
6.	5.28	170.00	39.210	23.06	0.2998	-0.5232
7.	5.50	168.16	39.440	23.45	0.3064	-0.5137

TABLE 16

Back extraction of metal ion from organic phase (Toluene) into 3.0M-HCl containing aqueous phase

S.No.	pH at which extraction to the organic phase occurred (ppm)	Concentration of organic phase (ppm)	Concentration of aqueous phase after back extraction (ppm)	% Back extraction	Distribution coefficient, D	$Log_{10}(D)$
1.	4.29	170.88	52.4	30.66	0.4423	-0.3543
2.	4.50	171.31	72.8	42.50	0.7390	-0.1313
3.	4.74	167.96	127.8	76.09	3.1823	0.5027
4.	4.88	171.13	105.7	61.76	1.6155	0.2083
5.	5.12	169.22	132.8	78.48	3.6463	0.5618
6.	5.28	171.68	109.5	63.78	1.7610	0.2458
7.	5.50	170.87	166.9	97.68	42.0403	1.6237

TABLE 17

Study of the Synergistic effect of 2,2′-bipyridine and 1,10-phenanthroline on the extraction of Cu(II) ion ($1.0\text{x}10^{-2}$M) with Ligand ($5.0\text{x}10^{-2}$M) at constant pH 5.90 into different solvents

S.No	Solvent	% Extraction in to		Distribution coefficient (D)		$Log_{10}(D)$	
		Bipyridine	Phenanthroline	Bipyridine	Phenanthroline	Bipyridine	Phenanthroline
1.	Toluene	96.75	79.91	29.76	3.9784	1.4737	0.5997
2.	Xylene	89.85	79.79	8.8531	3.9478	0.9471	0.5964
3.	Kerosene	81.18	79.52	4.3142	3.8831	0.6349	0.5892
4.	Chloroform	85.28	84.69	5.7959	5.5319	0.7631	0.7429
5.	Carbontetrachloride	-	79.57	-	3.8960	-	0.5906

TABLE 1[illegible]

Extraction of 1.0 x 10^{-2}M Cu(II) with 5.4 x 10^{-2} M Schiff base as a function of pH into Kerosene

S.No	pH	% Extraction	Distribution coefficient (D)	Log_{10} (D)
1.	4.29	80.46	4.1184	0.6147
2.	4.50	94.66	17.725	1.2486
3.	4.74	97.87	46.0477	1.6632
4.	4.88	99.54	216.4974	2.3354
5.	5.12	99.66	289.8843	2.4622
6.	5.28	99.09	104.4761	2.0190
7.	5.50	99.75	396.3978	2.5981

TABLE 19

Back extraction of metal ion from organic phase (Kerosene) into 4.0M - HCL containing aqueous phase

S.No	pH	Concentration of organic phase after extraction (ppm)	Concentration of aqueous phase after back extraction (ppm)	% Extraction	Distribution Coefficient D	$\text{Log}_{10}(D)$
1	4.29	180.80	47.1	26.05	0.3523	-0.4531
2	4.50	212.70	28.7	13.49	0.1560	-0.8069
3	4.74	219.92	59.2	26.92	0.3683	-0.4337
4	4.88	212.82	29.7	13.96	0.1622	-0.7900
5	5.12	213.06	13.6	06.38	0.0682	-1.1663
6	5.28	211.77	11.57	5.46	0.0578	-1.2381
7	5.50	213.26	18.96	8.89	0.0976	-1.0106

TABLE 20

Absorbance at λ_{max} to check the effect of 5.0 ml of interferring ion into 5.0 ml (5.0 x 10^{-2}M) Triazole + 5.0 ml (1.0 x 10^{-2}M) Cu(II) soln. with reference to solution containing, 5.0 ml of Cu(II) + 5 ml of triazole + 5 ml of water

S.No.	Salt	Concentration of interferring ion (M) in solution	Absorbance at λ_{max}	
			348.0 nm	512.0 nm
1	$BaCl_2.2H_2O$	0.5M	0.184	0.266
		0.1M	0.321	0.264
2	$Co(NO_3)_2.6H_2O$	1.0M	0.165	2.275
		0.1M	0.333	0.733
3	KCl	1.0M	0.201	0.270
		0.1M	0.218	0.149
4	$ZnSO_4$	0.5M	0.407	2.282
		0.1M	0.069	0.141
5	Ferrous ammonium sulphate	0.05M	0.470	1.190
6	$NiSO_4.H_2O$	1.0M	0.281	0.195
		0.1M	0.135	0.239
7	$Pb(NO_3)_2$	0.5M	0.266	0.253
		0.1M	0.143	0.240
8	$Ag(NO_3)_2$	1.0M	0.335	2.204
		0.1M	0.074	1.717
9	Na_2HPO_4	0.1M	0.291	0.129

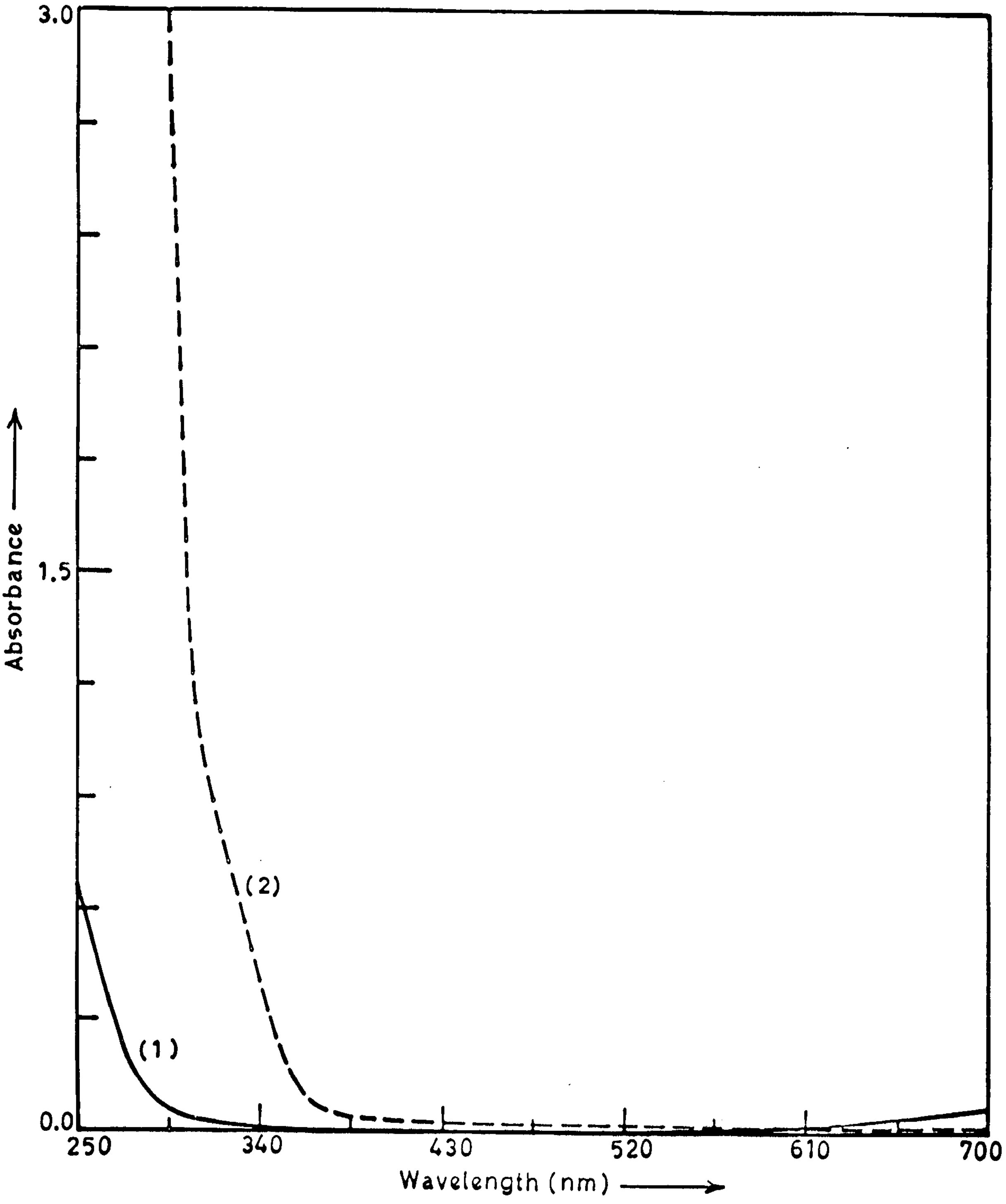


Fig.2: 1) ELECTRONIC SPECTRUM OF $5.0X10^{-2}M$ TRIAZOLE IN WATER WITH REFERENCE TO WATER.

2) ELECTRONIC SPECTRUM OF $1.0X10^{-2}M$ Cu(II) SOLUTION WITH REFERENCE TO WATER.

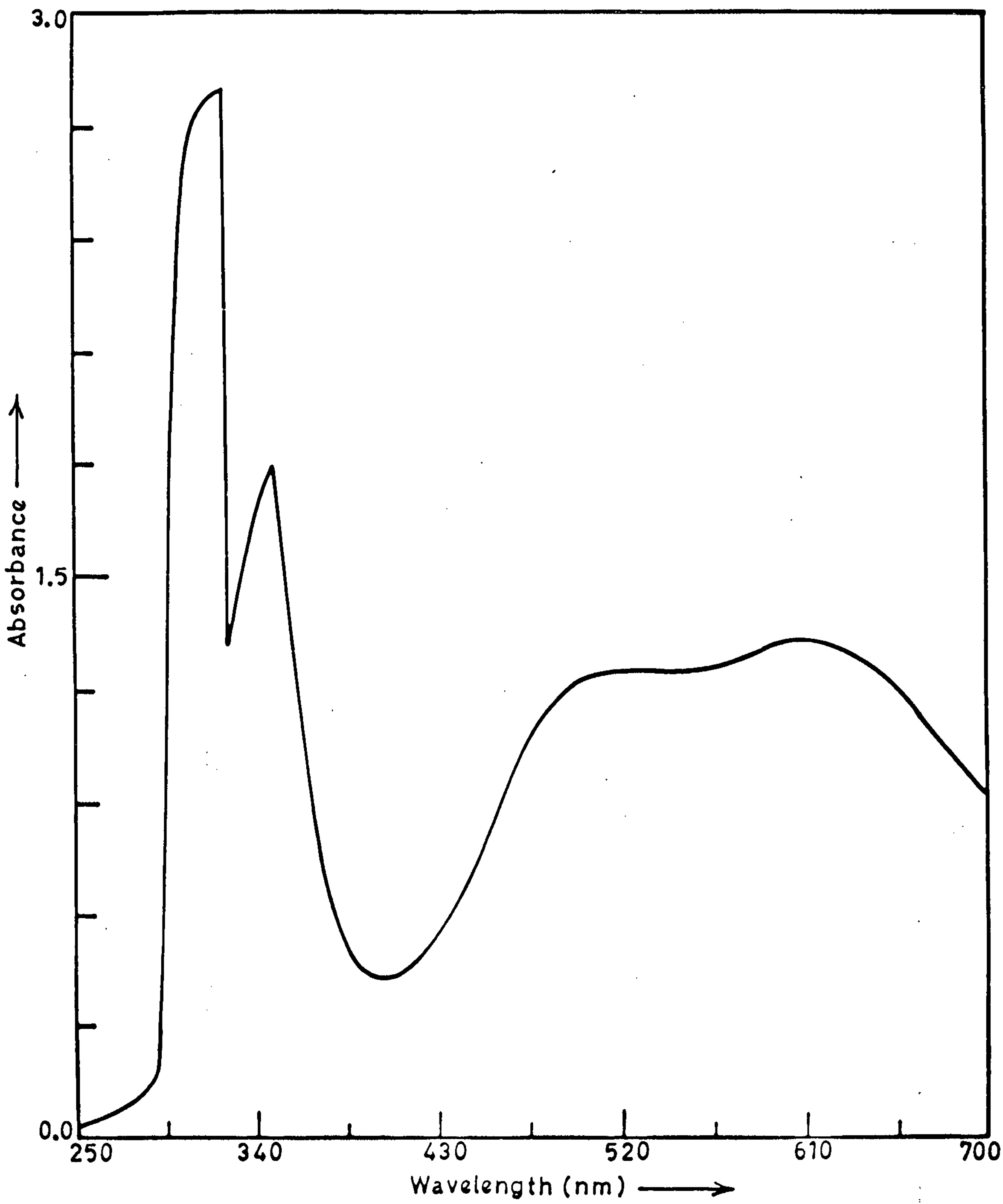


FIG.3: ELECTRONIC SPECTRUM OF COMPLEX [Cu(II)(1.0X10^{-2}M) - TRIAZOLE (5.0X10^{-2}M)] IN H_2O vs. A REAGENT BLANK [TRIAZOLE (5.0X10^{-2}) + WATER].

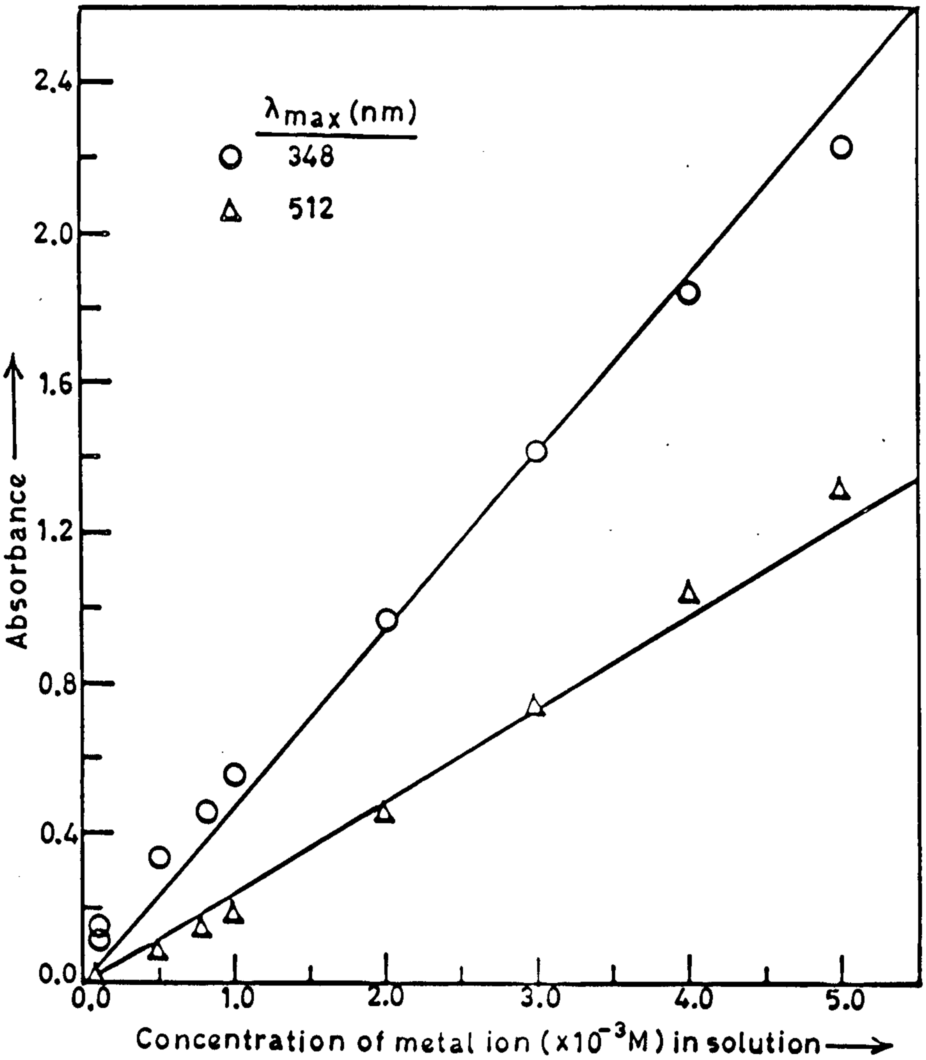


FIG.4: CALIBRATION CURVE OF Cu(II) ION OF CONCENTRATION 0.08×10^{-3}M - 5.0×10^{-3}M IN SOLUTION, WITH LIGAND (5.0×10^{-2}M) CONCENTRATION 25×10^{-3}M IN SOLUTION TO VERIFY BEER'S LAW AT λ_{max} 348.0 nm AND 512.0 nm.

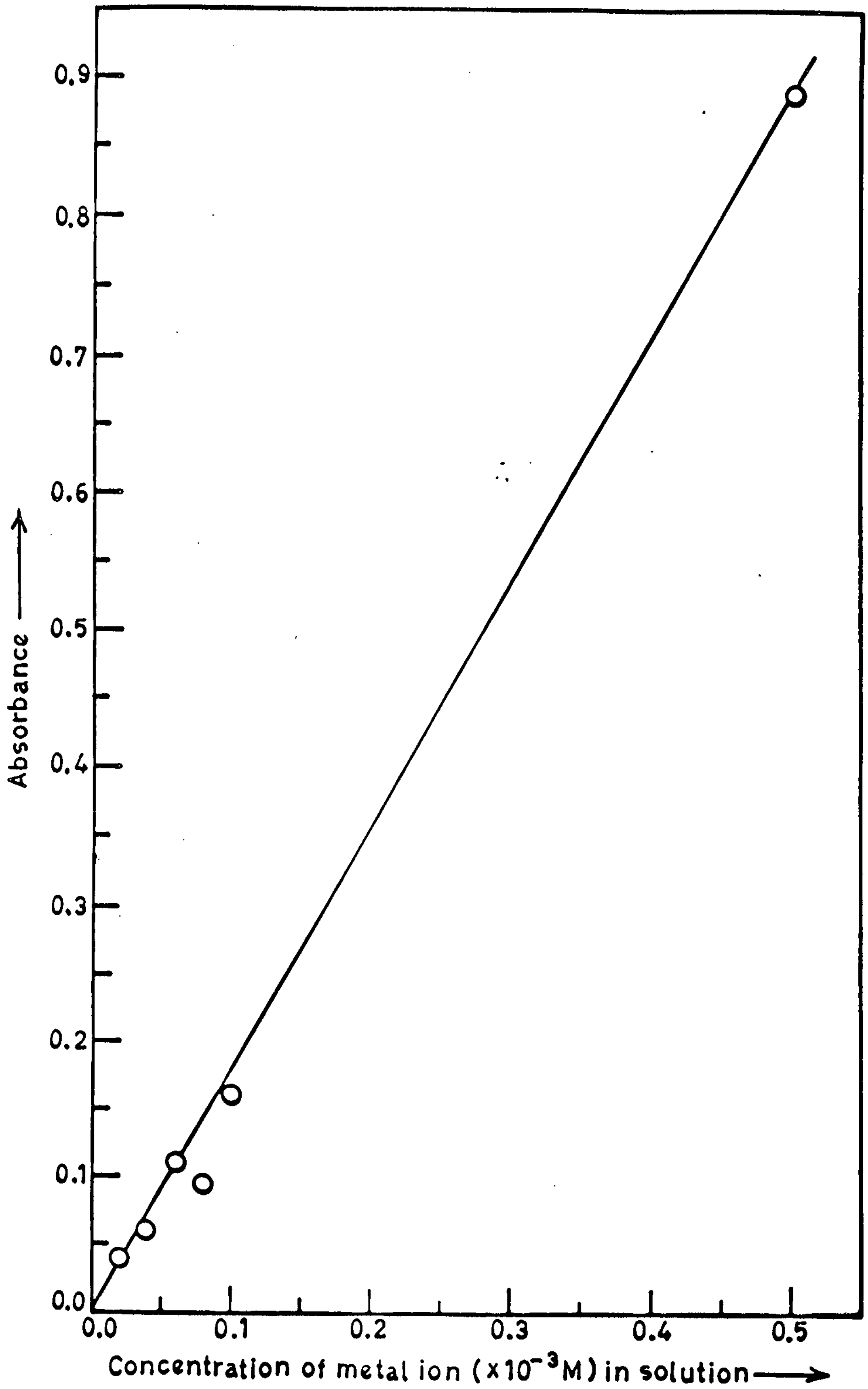
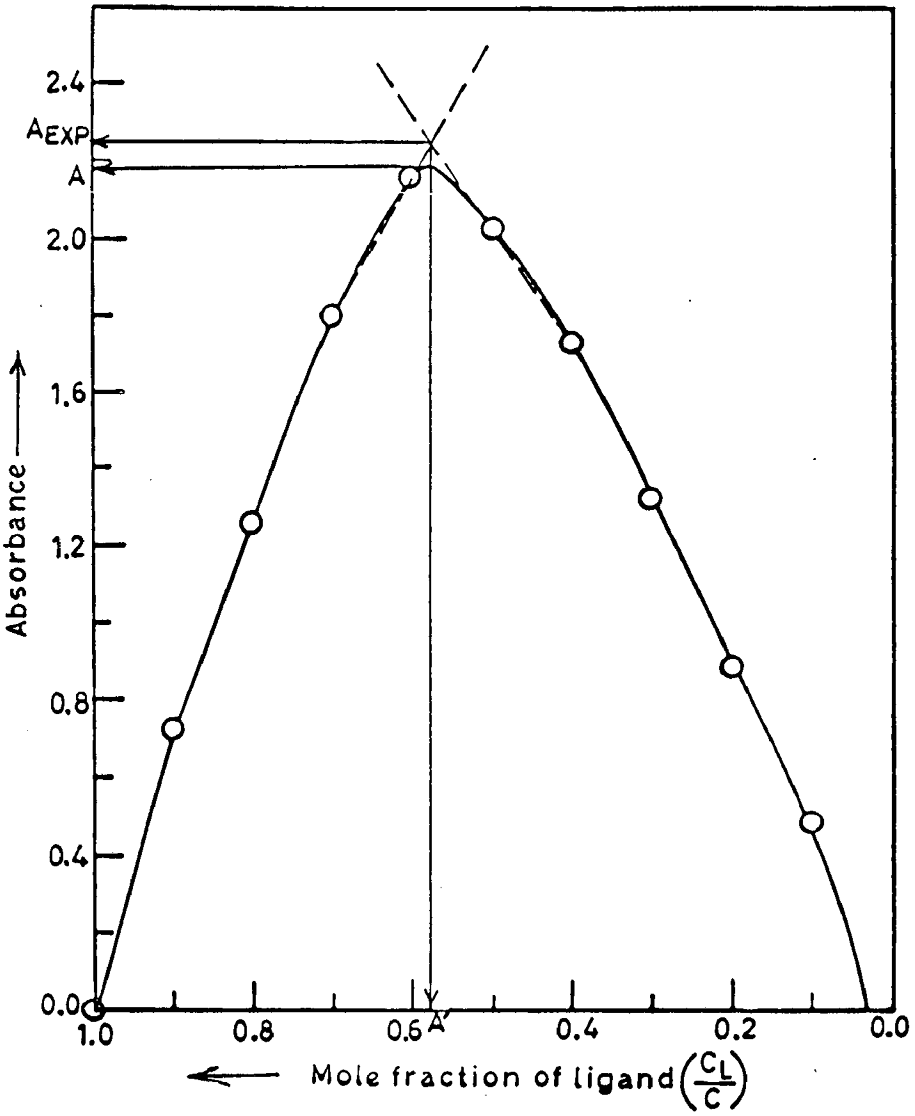


FIG. 5: CALIBRATION CURVE OF Cu(II) ION OF CONCENTRATION 0.02x10^{-3}M - 0.5x10^{-3}M IN SOLUTION, WITH LIGAND (5.0x10^{-2}M) CONCENTRATION 2.5x10^{-3}M IN SOLUTION TO VERIFY BEER'S LAW AT λ_{max} 336.0 nm.



5: DETERMINATION OF STABILITY CONSTANT AND COMPOSITION OF THE COMPLEX FORMED USING JOB'S CONTINUOUS VARIATION METHOD AT λ_{max} 336.0 nm.

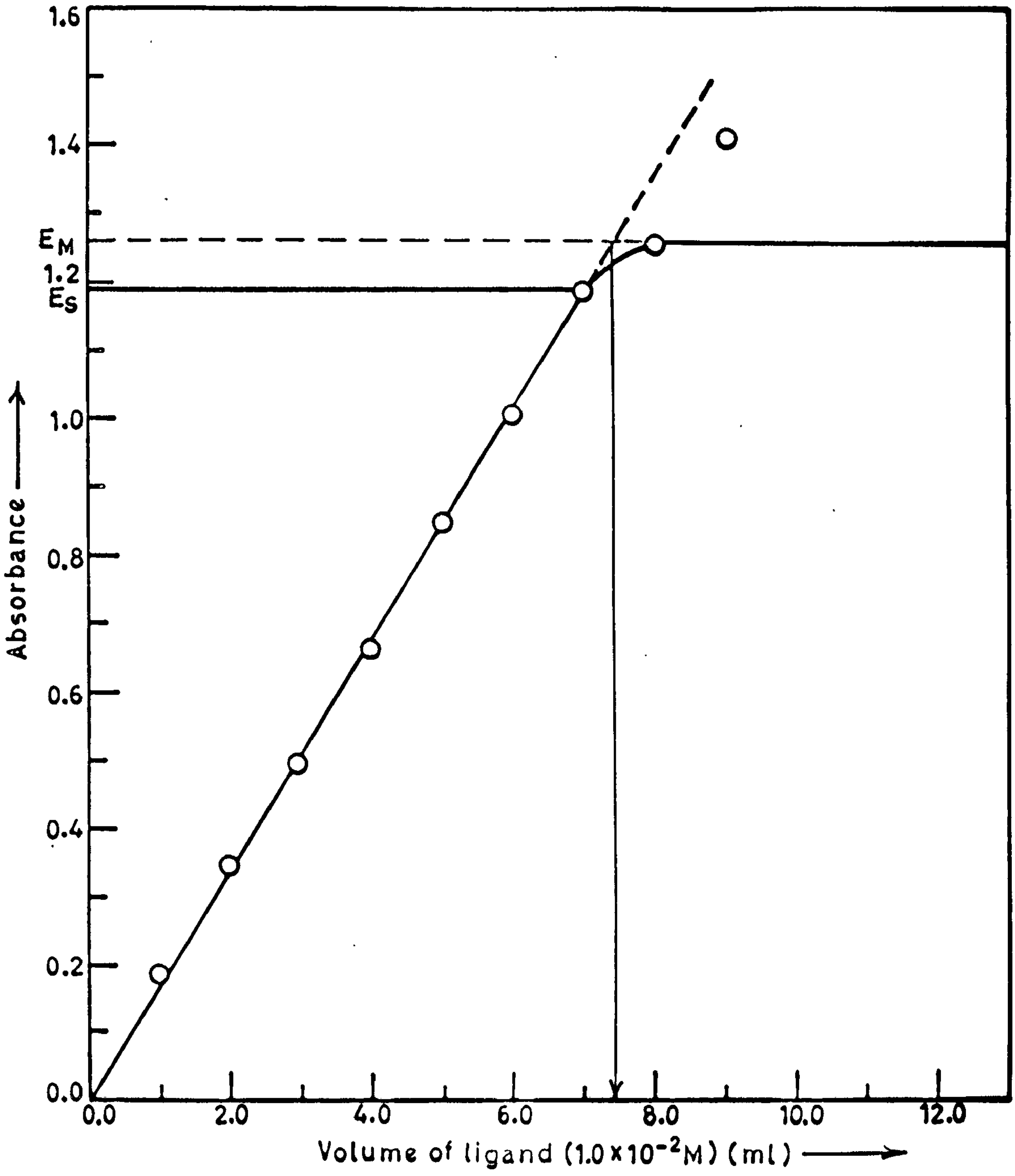


FIG. 7: DETERMINATION OF STABILITY CONSTANT AND COMPOSITION OF COMPLEX USING MOLAR RATIO METHOD AT CONSTANT METAL ION, Cu(II) CONCENTRATION OF 1.0×10^{-2} M [0.33×10^{-2} IN SOLUTION] AT λ_{max} 348.0 nm.

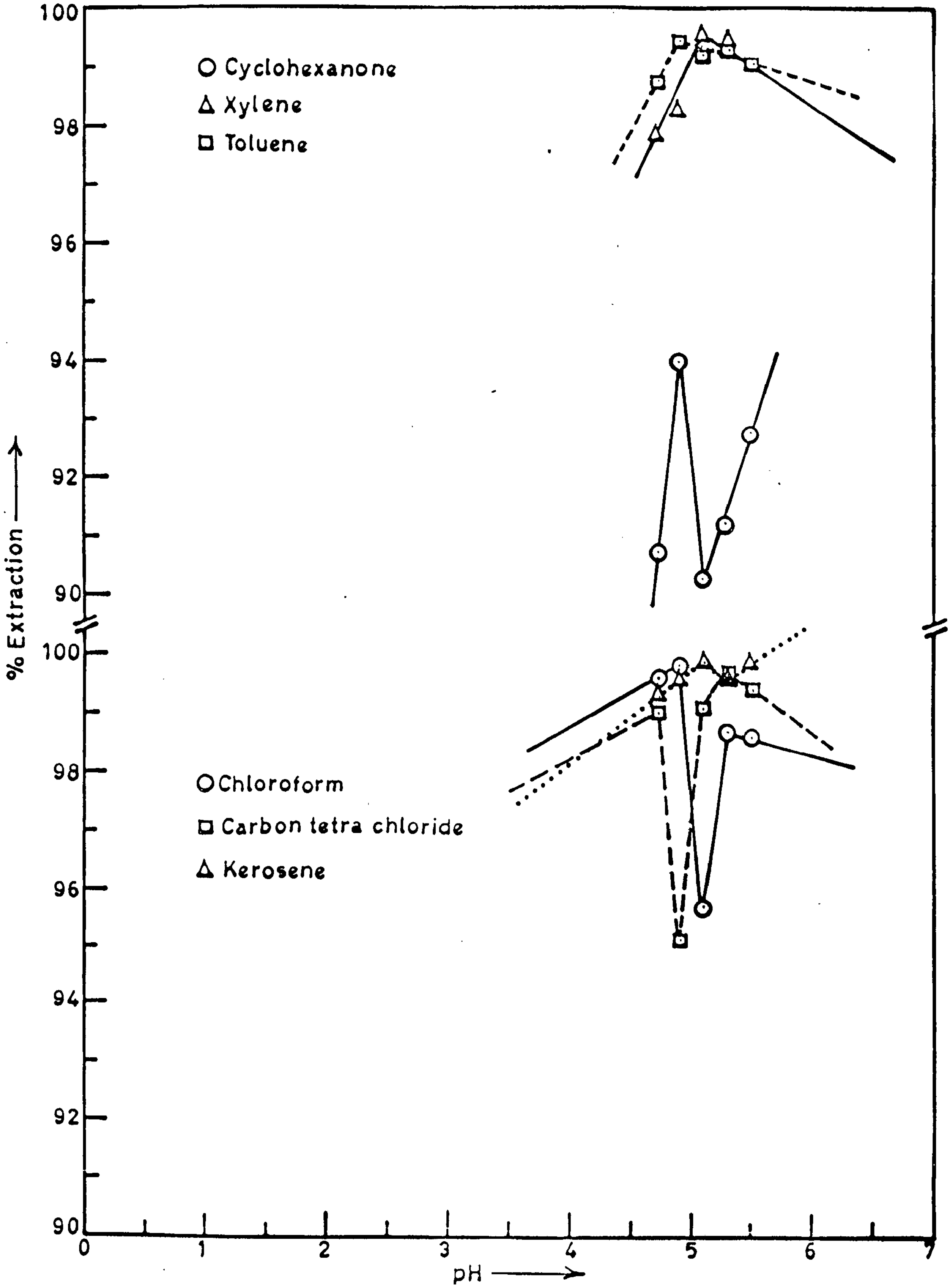


FIG. 8: EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION OF Cu(II) AT CONSTANT LIGAND (5.0×10^{-2}M) AND METAL ION (1.0×10^{-2}M) CONCENTRATION INTO DIFFERENT DILUENTS.

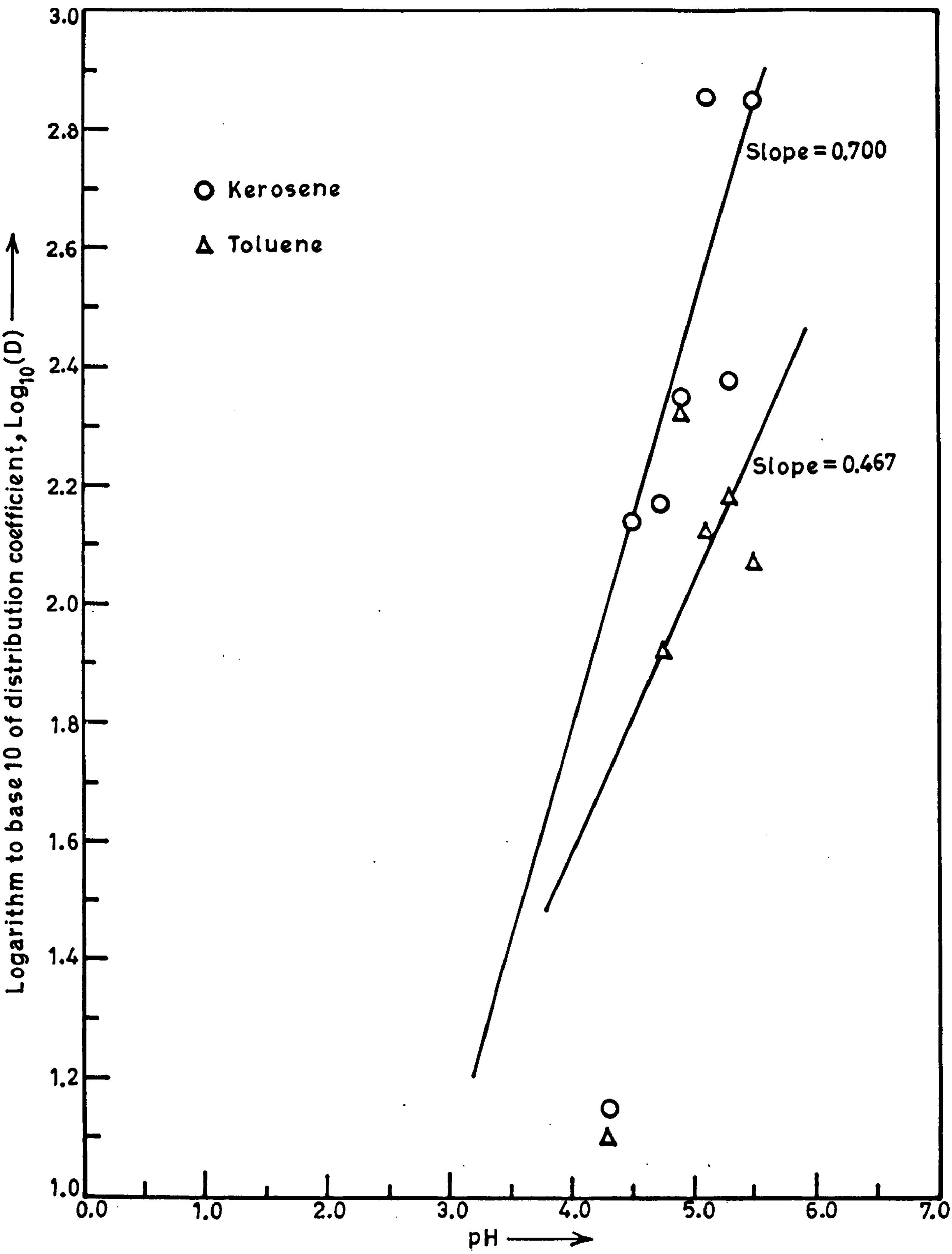


FIG.9: EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION OF Cu(II) AT CONSTANT LIGAND CONCENTRATION (5.0×10^{-2}M) AND METAL ION CONCENTRATION (1.0×10^{-2}M) INTO KEROSENE AND TOLUENE.

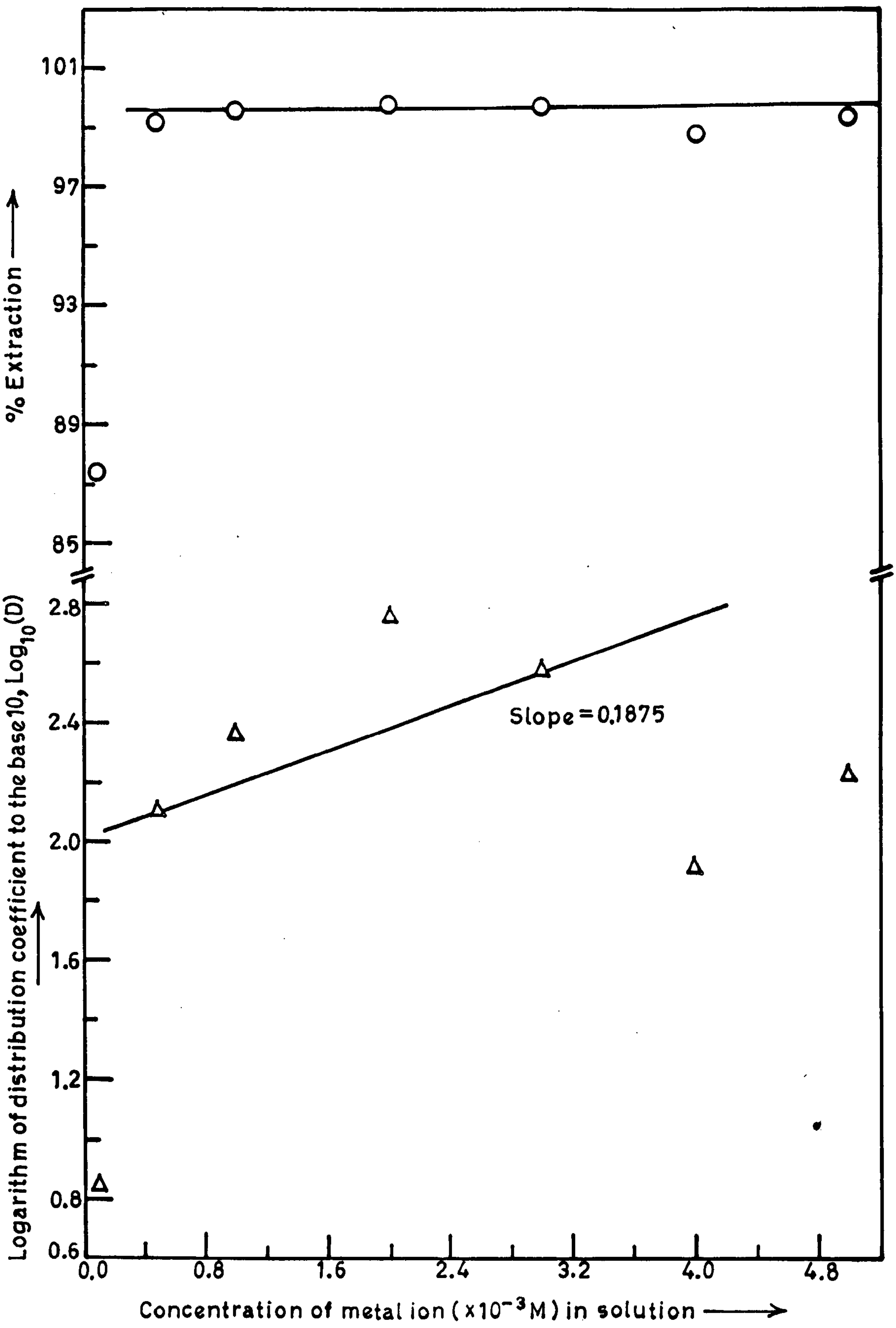


FIG. 10: EFFECT OF METAL ION CONCENTRATION ON THE EXTRACTION OF Cu(II) AT CONSTANT pH AND LIGAND CONCENTRATION (5.0×10^{-2}M) INTO KEROSENE.

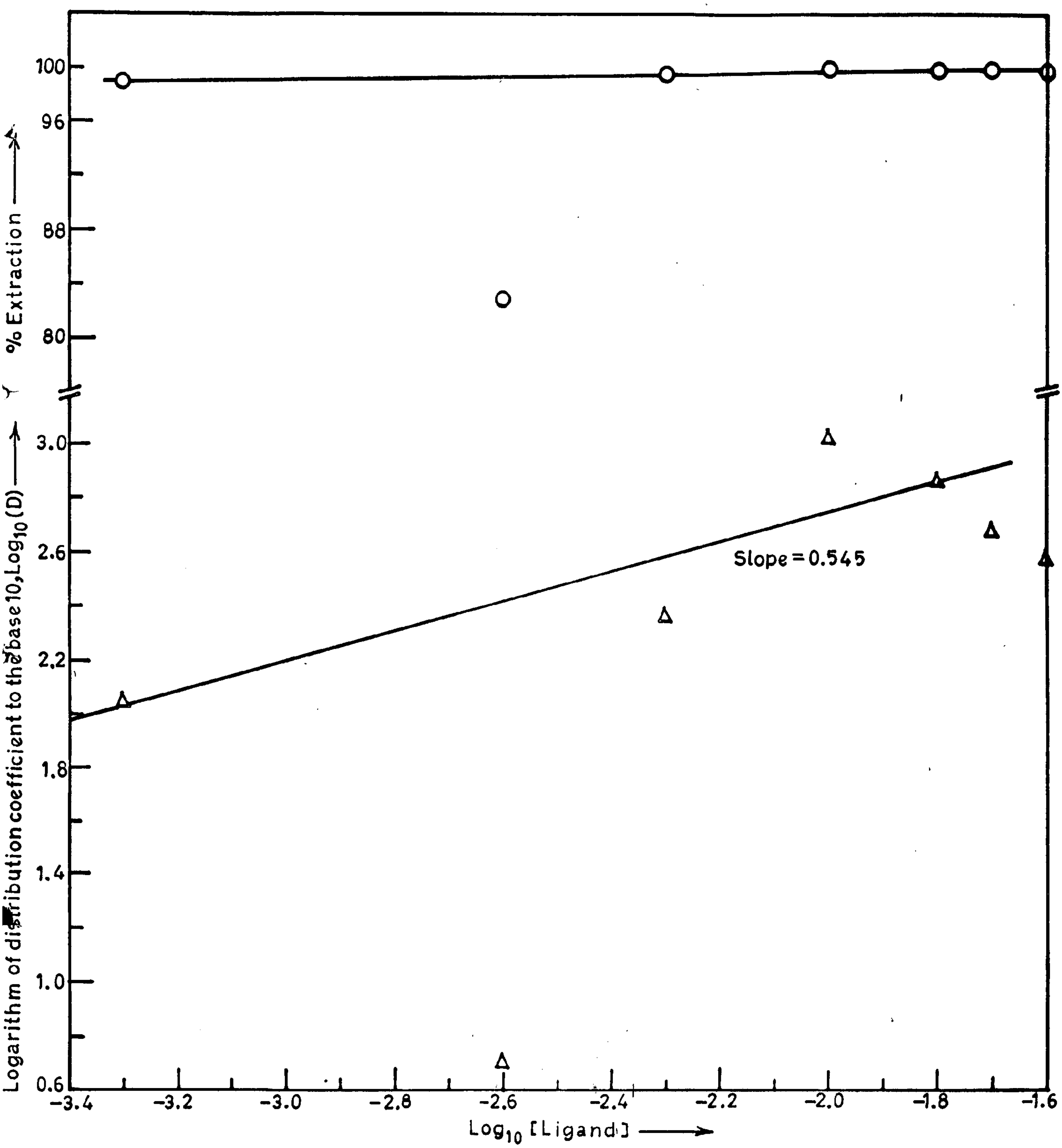


FIG. 11: EFFECT OF LIGAND CONCENTRATION ON THE EXTRACTION OF Cu(II) ION FROM THE AQUEOUS PHASE AT CONSTANT pH AND METAL ION CONCENTRATION (1.0×10^{-2}M) INTO KEROSENE.

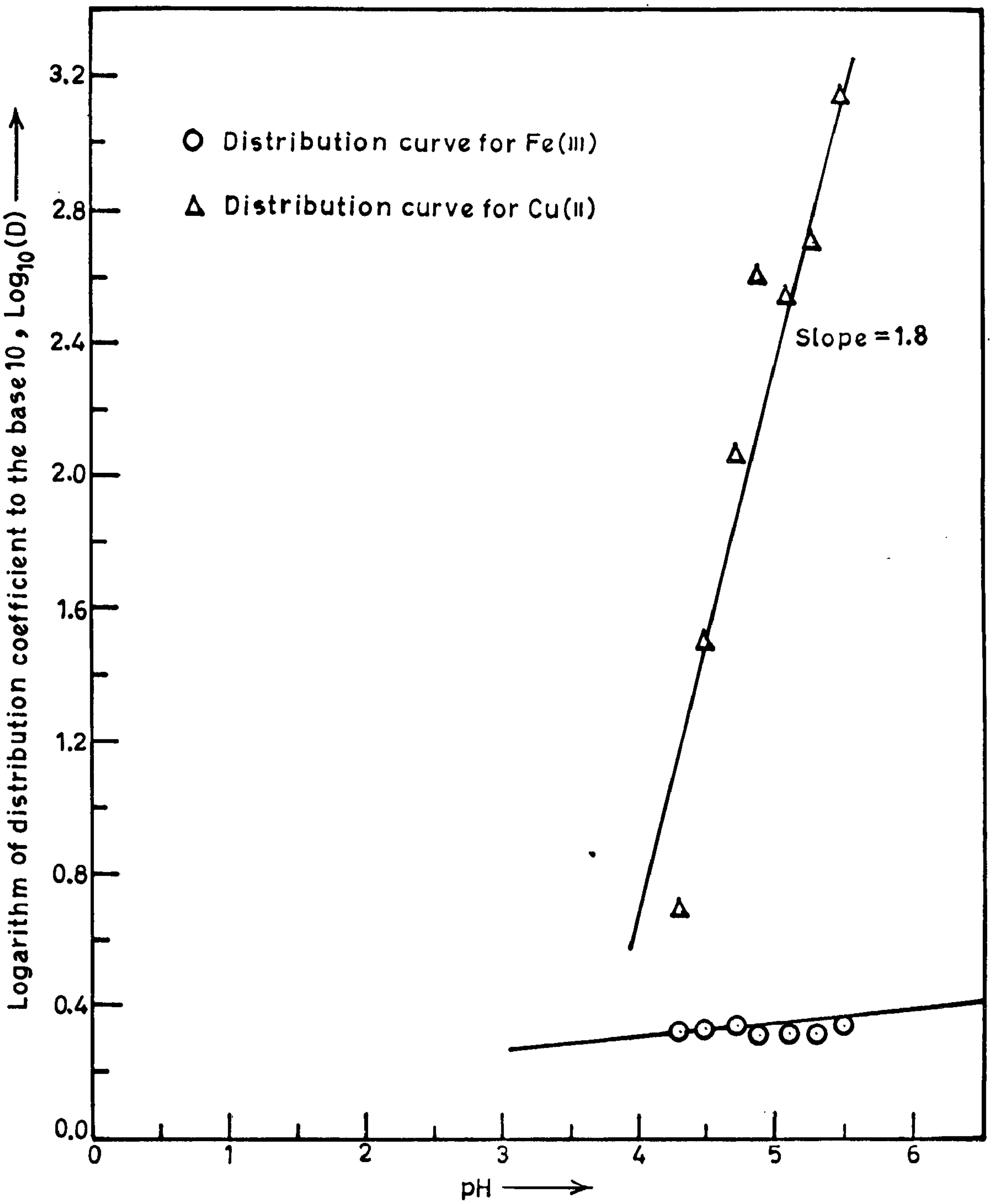


FIG.12: EFFECT OF INTERFERRING METAL ION FOR THE EXTRACTION OF Cu(II) AT CONSTANT (1.0×10^{-2}M) METAL ION AND (5.0×10^{-2}M) LIGAND CONCENTRATION AS A FUNCTION OF pH INTO KEROSENE.

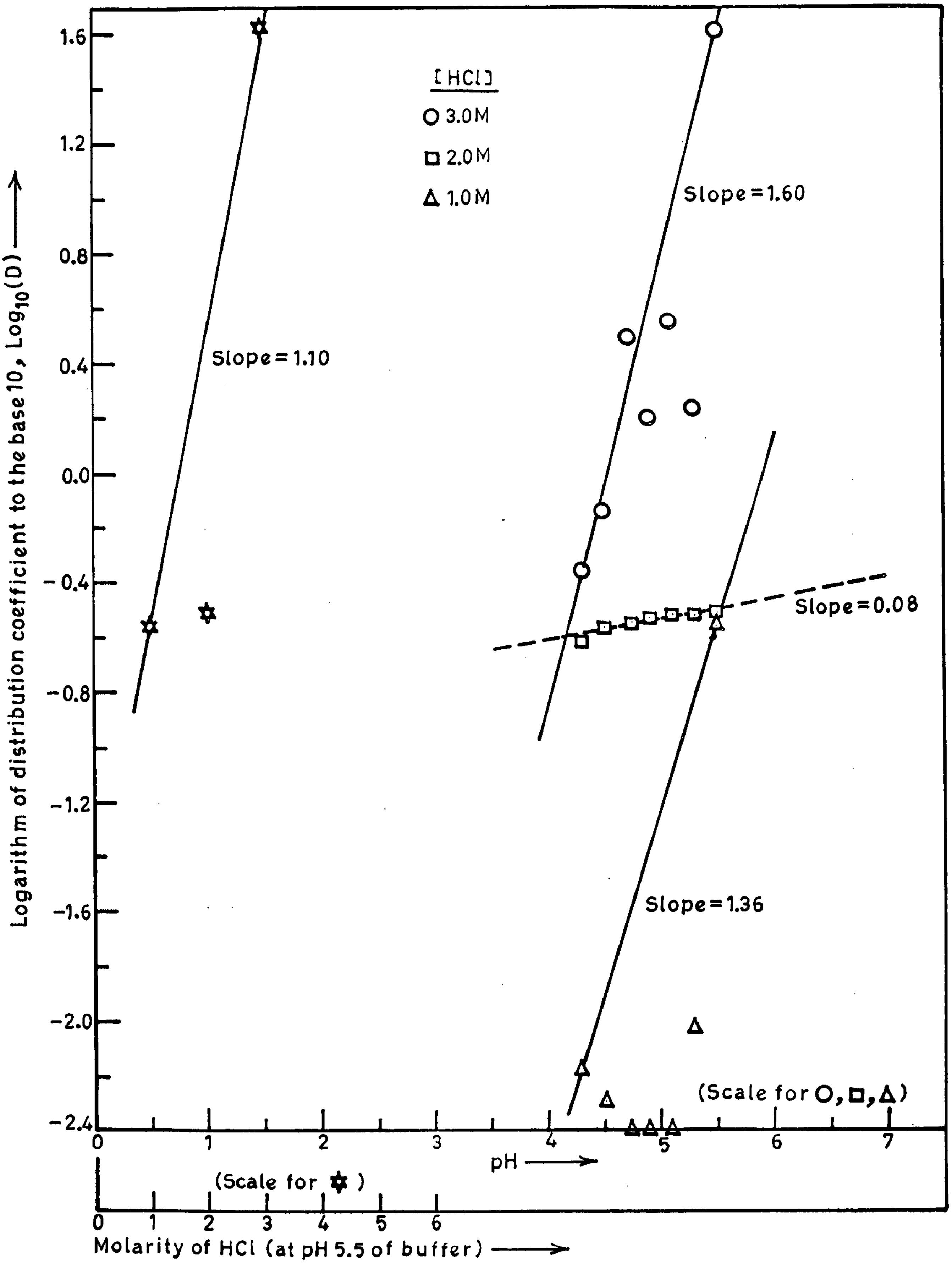


FIG.13: BACK EXTRACTION OF METAL ION FROM ORGANIC PHASE (TOLUENE) INTO AQUEOUS PHASE CONTAINING HCl OF SPECIFIC MOLARITY AS A FUNCTION OF pH (AT WHICH EXTRACTION TO THE ORGANIC PHASE OCCURRED).

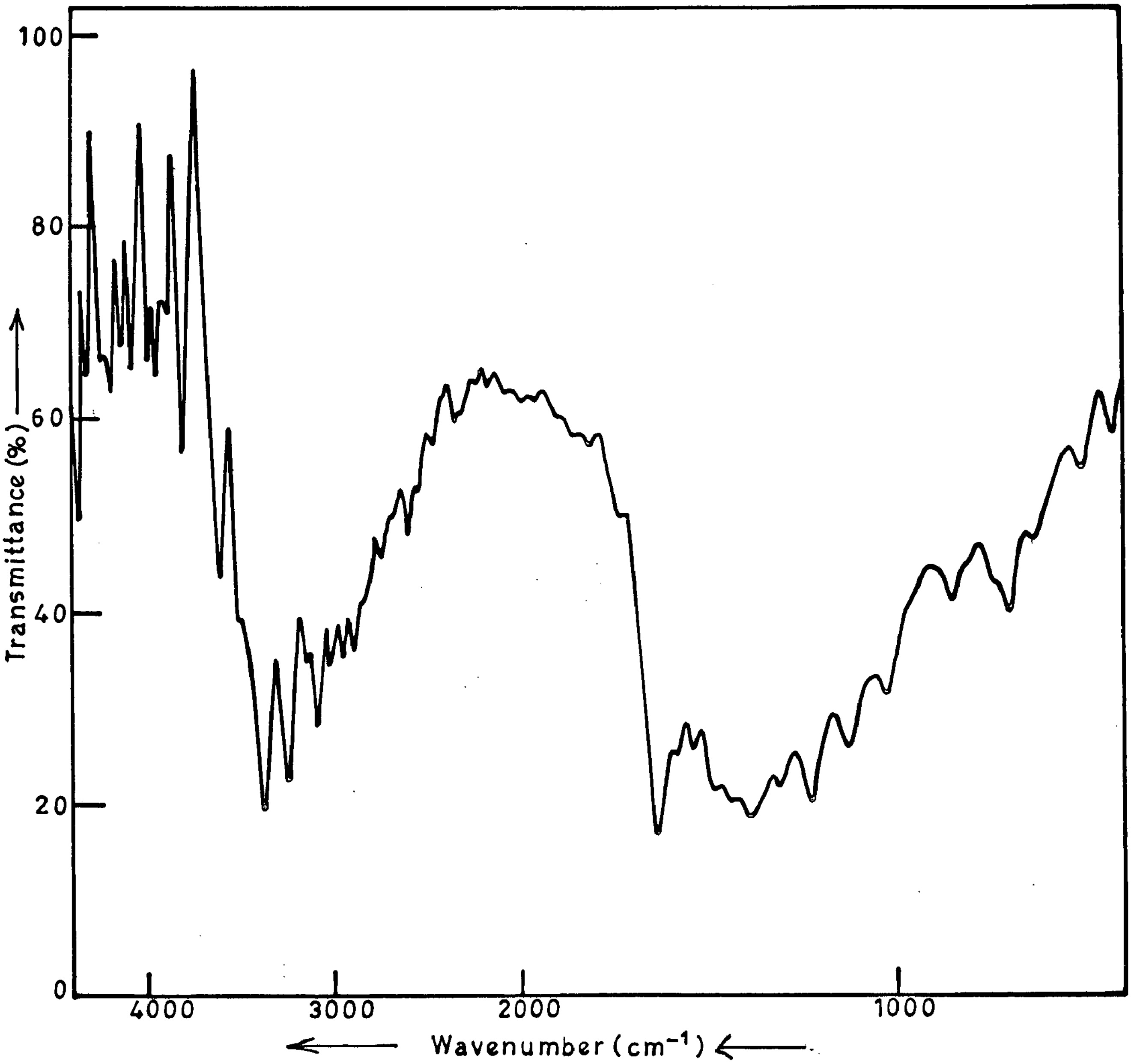


FIG.14: **INFRARED SPECTRUM OF SCHIFF BASE DERIVED FROM SALICYLALDEHYDE AND 3-AMINO-5-MERCAPTO-1,2,4-TRIAZOLE USING FTIR INSTRUMENT.**

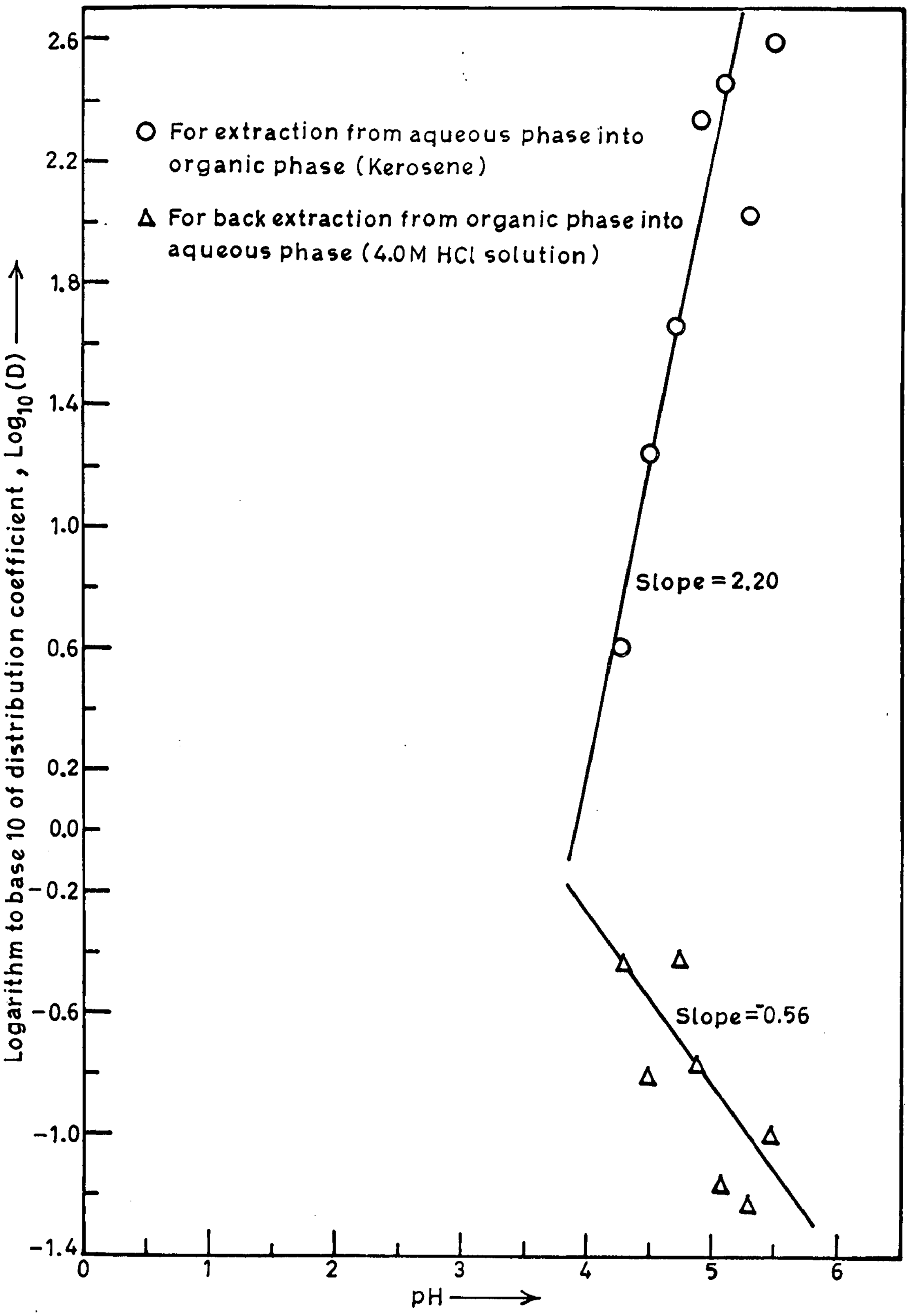


FIG.15: 1) EFFECT OF pH OF THE AQUEOUS PHASE ON THE EXTRACTION OF Cu(II) AT CONSTANT METAL ION ($1.0X10^{-2}$M) AND LIGAND i.e. SCHIFF BASE ($5.4x10^{-2}$M) CONCENTRATION INTO KEROSENE.

2) EFFECT OF pH ON THE BACK EXTRACTION OF Cu(II) FROM ORGANIC PHASE (KEROSENE) INTO AQUEOUS PHASE CONTAINING 4.0M-HCl SOLUTION.

REFERENCES

1. W.C. Cooper, Systematic Analytical Chemistry of Copper (Ed. Kolthoff, Elving and Sandell, Treatise on Analytical chemistry) Interscience Publishers, New York, 1961,p.2
2. F.A. Cotton and G. Wilkinson, Advanced Inorganic chemistry, 3rd Ed., Wiley Eastern limited , New Delhi, 1972, p.905.
3. J. D. Lee, Concise Inorganic Chemistry, 4th Ed., Chapman & Hall, London, 1991, p.818,832-833.
4. R.E. Treybal, Liquid Extraction,2nd Ed., Mc Graw-Hill Book Company, Incl., New York, 1963,p.122,561.
5. P.B.Janardhan, Physico-Chemical Techniques of Analysis Vol.II, Asia Publishing House, Bombay, 1973, p.563.
6. G.D.christian, Analytical Chemistry, 2nd Ed., Xerox College Publishing, Massachusetts, 1971,p.95.
7. J.Rydberg,H.Reinhardt and J.O. Liljenzin,Experience with the AKUFVE Solvent Extraction Equipment, (Ed. J.A.Marinsky and Y. Marcus, Ion Exchange and Solvent Extraction, Vol.III) Marcel Dekker , Inc.,New York,1973, p.111.
8. G.H. Jeffery , J. Bassett, J.Mendham and R.C.Denney, Vogel's Textbook of Quantitative Chemical Analysis, 5th Ed.,Longman, 1989, p.164,167.
9. Y.Marcus and A.S. Kertes, Ion Exchange and Solvent Extraction of Metal Complexes, 1st Ed., Wiley-Interscience Ltd.,1969,p.431.
10. H.Matsunaga and T.M.Suzuki, Chem.Lett., 2,225(1986);A.A.,48,9B210 (1986).

11. M.Vackova and M.Petro, Chem.Pap.,40, 247(1986);A.A.,48,10B13 (1986).

12. G.S. Desai and V.M. Shinde, Fresenius'J.Anal.Chem., 336, 575 (1990); A.A., 53, 3D25 (1991).

13. I. Karadyova, S. Arpadyan, P.Mandyukov and T.Deligeorgiev, Analyst (London), 115, 1539 (1990); A.A., 53, 11D17 (1991).

14. T. Katami, T. Hayakawa, M.Furukawa, S.Shibata, Analyst (London), 109, 1511 (1984); A.A., 47, 7B30 (1985).

15. V.M. Shinde, Indian J. Chem., Sect. A, 27A, 921 (1988); A.A., 51, 7B25 (1989).

16. R. Saran, T.S. Basu Baul, P. Srinivas and D.T. Khathing, Anal. Lett, 25, 1545 (1992); A.A., 55, 5H52 (1993).

17. X.N. Ge, P.F. Jiang and W.S. Bo, Fenxi Huaxue, 22, 863 (1994); A.A., 57, 3D44 (1995).

18. D.V. Khasnis and V.M. Shinde, J.Indian Chem. Soc., 61, 275 (1984); A.A., 47, 6B127 (1985).

19. A.V. Reddy and Y.K. Reddy, Talanta, 33, 617 (1986); A.A., 48, 10B37 (1986).

20. N.S.R. Reddy and D.V. Reddy, Acta Cienc. Indica, Chem., 16C, 241 (1990); A.A., 54, 5D30 (1992).

21. J.-S. Lee, K. Uesugi and T. Nagahiro, Anal. Proc. (London), 32, 65 (1995); A.A., 57, 4D7 (1995).

22. S.Inone, H. Inai, S. Hoshi and M. Matsubara, Anal. Sci., 1, 423 (1985); A.A., 48, 8B35 (1986).

23. K.Haraguchi, M. Nishida, A.Ayame, M. Murozumi, T.Saitoh and H. Watanabe, Anal. Sci., 5, 735 (1989); A.A., 52, 10B3 (1990).

24. F. Salinas, M. Jimenez-Arrabal and I. Duran Meras, Proc. Indian Acad. Sci., Chem. Sci., 97, 159 (1986); A.A., 49, 8A5 (1987).

25. N.R. Biswas, B.C. Ray and S. Lahiri, J. Indian Chem. Soc., 60, 775 (1983); A.A., 47, 1B187 (1985).

26. M. Ines Toral and P. Richter, Anal. Lett., 28, 1083 (1995); A.A., 57, 7D30 (1995).

27. K.Hayashi, Y. Sasaki, S. Tagashira, S. Inomata, J.Rikitak, Y. Hisatomi and M. Suzuki, Bunseki Kagaku, 33, 247 (1984); A.A., 47, 1B172 (1985).

28. J.B. Beferull and M.De la Guardia Cirugeda, Afinidad, 41, 274 (1984); A.A., 47, 2H36 (1985).

29. S. Ichinoki and M. Yamazaki, Anal. Chem., 57, 2219 (1985); A.A., 48, 6D46 (1986).

30. S.C. Apte and A.M. Gunn, Anal. Chim. Acta, 193, 147 (1987); A.A., 50, 3H36 (1988).

31. M.Murakami and T. Takada, Talanta, 39, 1293 (1992), A.A., 55, 7D81 (1993);Talanta, 37, 229 (1990); A.A., 53, 3A20 (1991).

32. K. Yoshida, S. Miyakoshi and T. Hasegawa, Shokuhin Eiseigaku Zasshi, 29, 249 (1988); A.A., 51, 4F2 (1989).

33. S.A. Popova, S.P. Bratinova and C.R. Ivanova, Analyst (London), 116, 525 (1991); A.A., 54, 1D161 (1992).

34. V.R. Patil, R.B. Kharat and B.R. Deshmukh, Chem. Anal. (Warsaw), 29, 113 (1984); A.A., 47, 5B26 (1985).

35. S.Ide and M. Takagi, Anal. Sci., 6, 599 (1990); A.A., 53, 11D2 (1991).

36. H.Itabashi, H. Kawamoto and H. Akaiwa, Bunseki Kagaku, 42, 693 (1993); A.A., 56, 5D54 (1994).

37. A.M. Kiwan, F. Hayder and F. Hassan, Anal. Chim. Acta, 182, 245 (1986); A.A., 49, 3A11 (1987).

38. D. Atanassova, A.N. Shishkov, N.D. Yordanov and M. Zolravkova, Izv. Khim., 23, 545 (1990), A.A., 54, 6D62 (1992).

39. A. Okhi, M. Takagi and K. Ueno, Anal. Chim. Acta, 159, 245 (1984); A.A., 47, 2B30 (1985).

40. E.Sekido, K. Chayama and H. Imamoto, Anal. Sci., 4, 511 (1988); A.A., 51, 3B38 (1989).

41. K. Chayama and E. Sekido, Anal. Chim. Acta, 248, 511 (1991); A.A., 54, 8D33 (1992).

42. K. Saito, I. Taninaka, S. Murakami and A. Muromatsu, Anal. Chim. Acta, 299, 137 (1994); A.A., 57, 6D4 (1995).

43. S. Abe, Y. Nakajima, M. Endo and T. Sone, Mikrochim. Acta, 3, 171 (1990); A.A., 54, 1D39 (1992).

44. B.K. Puri, M. Katyal, M. Satake and L.F. Chang, Indian J. Chem., Sect. A., 27A, 558 (1988); A.A., 51, 1B36 (1989).

45. S.Q. R. Ilyas and A.P. Joshi, Indian J. Chem., Sect. A., 22A, 907 (1983); A.A., 47, 3B25 (1985).

46. A. Desai and H.B.Naik, J. Inst. Chem. (India), 63, 48 (1991); A.A., 54, 9E17 (1992).

47. A.T. Rane and D.R. Nepali, Asian J. Chem., 2, 43 (1990); A.A., 53, 12D16 (1991).

48. N. Egashira, M. Takagi and M. Maeda, Anal. Sci., 7, 907 (1991); A.A., 54, 10D43 (1992).

49. K.V.Reddy and R.C. Hussain, Curr. Sci., 53, 798 (1984); A.A., 47, 1B35 (1985).

50. K. Uesugi, T. Nagahiro, T. Kumagai and S. Yamaguchi, Kenkyu Hokoku-Himeji Kogya Daigaka, 39(A), 16, (1986); A.A., 49, 11B51 (1987).

51. V. Ramesh and G.N. Rao, Indian J. Technol., 25, 418 (1987); A.A., 50, 7B22 (1988).

52. A.Jyothi and G.N. Rao, Proc.-Indian Acad. Sci., Chem. Sci., 100, 455 (1988); A.A., 52, 1B7 (1990).

53. M. Spankova and L. Smirnova, Chem. Listy, 85, 212 (1991); A.A., 54, 3D15 (1992).

54. E. Kimura, C.A. Dalimunte, A. Yamashita and R. Machida, J. Chem. Soc., Chem. Commun., 15, 1041 (1985); A.A., 48, 1B49 (1986).

55. T. Morimoto, S. Ochiai and T. Sekine, Anal. Sci., 4, 255 (1988); A.A., 51, 5B35 (1989).

56. K. Ueda, S. Kitahara, K. Kubo and Y. Yamamoto, Bunseki Kagaku, 36, 728 (1987); A.A., 50, 3H53 (1988).

57. J.F. Da Silva and W. Martins, Talanta, 39, 1307 (1992); A.A., 55, 7D18 (1993).

58. K. Ueda, K. Kubo, O. Yoshimura and Y. Yamamoto, Bull. Chem. Soc. Jpn., 61, 2791 (1988); A.A., 51, 1H33 (1989).

59. E. Kavlentis, Mikrochim. Acta, III, 251 (1987); A.A., 50, 3A10 (1988).

60. J.A. Stratis, D.G. Themelis, D.G. Zatkas and I.A. Kafritsas, Anal. Lett., 22, 1779 (1989); A.A., 52, 4B13 (1990).

61. M.T. Siles Cordero, A. Garcia De Torres and J.M. Cano Pavon, Talanta, 40, 691 (1993); A.A., 55, 11D25 (1993).

62. X. Huang, Lihua Jianyan, Huaxue Fence, 27, 51 (1991); A.A., 54, 3H294 (1992).

63. A.M. Sastre, N. Miralles and M. Aquilar, Chem. Scr., 24, 44 (1984); A.A., 47, 5B27 (1985).
64. I.L. Dukov, Anal. Lab., 5, 219 (1996); A.A., 59, 8D14 (1997).
65. Y. Nagaosa and Y. Binghua, Talanta, 44, 327 (1997); A.A., 59, 6D89 (1997).
66. T.S. Lobana, P.K. Bhatia, M. Dua and S. Kaur, Indian J. Chem., Sect. A, 33A, 1046 (1994); A.A., 57, 7D39 (1995).
67. D. Atanasova and A.N. Shishkov, Zavod. Lab., 57, 17 (1991); A.A., 55, 3E27 (1993).
68. S.P. Arya, J.L. Malla and V. Slathia, Talanta, 34, 293 (1987); A.A., 49, 10B29 (1987).
69. B. Elman, A.G.S. Hogberg, M.Weber and M. Muhammed, Polyhedron, 4, 1197 (1985); A.A., 48, 6A5 (1986).
70. Y. Moriya, M. Sugai, Y. Ohshima and N. Ogawa, Anal. Sci., 12, 511 (1996); A.A., 59, 3D55 (1997).
71. H. Yamada, K. Yajima, Y. Noda and H. Wada, Anal. Sci., 12, 419 (1996); A.A., 59, 3D58 (1997).
72. H. Yamada, Y. Taguchi and H. Wada, Talanta, 41, 573 (1994); A.A., 56, 10D45 (1994).
73. S. Jimenez Gomez, M.I. Rico Selas and J.R. Tapia Morino, An. Quim., Ser. B, 80, 368 (1984); A.A., 47, 4B30 (1985).
74. K. Yamamoto and S. Motomizu, Anal. Sci., 5, 745 (1989); A.A., 52, 10B13 (1990).
75. H.W. Gao, Spectrochimj Acta, Part A, 51A 1379 (1995) A.A.57, 11D42(1995).
76. J.Yan, Z. Bei and M. Zhu, Fenxi Ceshi Tongbao, 9, 63(1990) ; A.A., 54, 4D44 (1992).

77. F. Hernandez Hernandez, M.T. Castillo, J.V. Sancho and J. Beltran, Analusis, 20 275 (1992) ; A.A., 55, 3D39 (1993).

78. S.C. Rui, S. Motomizu and K. Toei, Bunseki kagaku, 34, 643 (1985) ; A.A., 48, 2B38 (1986).

79. F. Capitan Garcia, L.F. Capitan Vallvey, D. Gines Fernandez Valdivia and P. Espinosa Hidalgo, Quim Anal., 7, 451 (1988); A.A., 52, 1B19 (1990).

80. A.Morales and L.Vallodores, Fresenius z. Anal. chem., 334, 53 (1989); A.A., 52, 3B22(1990).

81 A. Saorkar, T.K. Thokdor, P.K. Paria and S.K. Majundor, J. Indian chean. Soc. , 65, 742 (1988) ; A.A. , 51, 7B24 (1989).

82. J. Flanjak and A. Hodda, Anal. Chim. Acta., 172, 313(1985); A.A., 48, 5D39 (1986).

83. G. Rauret, L. Pineda , M. Ventura and R. Compano, Talanta , 33, 141 (1986);A.A., 48 , 10C24 (1986)

84. I.L .Dukov, Anal. Lab., 5, 147 (1996); A.A, 59, 3D15 (1997).

85. J.M. Castresana, M.P.Elizalde, M.Aguilan and M. Cox , Quim. Anal. (Barcelona), 5, 409(1986); A.A., 49, 11B43(1987).

86. S. Inokuma, K. Hasegawa, S. Sakai and J. Nishimura, Chem Lett., 9,1729(1994); A.A.,57,6D8(1995).

87. H.Stephan , K. Gloe, J. Berger and P.Muehl, Solvent Extr. Ion Exch.,9,459(1991); A.A., 55,2D4(1993).

88. N.Hirayama, S.Iimuro, K. Kubono, H. Kokusen and T.Honjo, Anal. Chim.Acta, 339, 115(1997); A.A., 59, 6D85 (1997).

89. L. Kostadinova, N. Elenkova and T. Nedeltcheva, Anal Lab.,4, 51(1995); A.A. , 57, 11H106(1995).

90. H.Satoh, Y. Kikuchi, K. Satoh, T. Suzuki and K. Sawada, Bunseki kagaku, 40, T119(1991); A.A., 54, 5D15(1992).

91. L.A.Pilipenko,L.L. Kolomiets, E.F. Gavrilova, Yu.M.Volovenko, A.G.Nemazany and V.V.Trachevskii,Zh. Anal. khim., 46,513 (1991);A.A.,54,4D50(1992).

92. V.D.Pillai and V.M.Shinde, Indian J.Chem, Sect.A,34A, 407(1995); A.A.,57, 10D46 (1995).

93. S.R. Kuchekar, M.A. Anuse and M.B.Chavan, Indian J. chem.,Sect A, 25A, 1041 (1986); A.A.,49, 9B24 (1987).

94. X.Sun,B.Li and K. Fu, Mikrochim. Acta, III, 101 (1990); A.A,53, 11D18(1991).

95. Yu.A. Zolotov,V.P Ionov,N.V. Niz'eva and A.A. Formanovskii,Dokl.Akad. Nauk SSSR, 277, 1145 (1984); A.A, 47, 5A16 (1985).

96. M Fujiwara, T. Matsushita, Y.Yamashoji, T. Morita, S.Tani, M.Tanaka and T. Shono, Bunseki Kagaku, 40,325 (1991); A.A, 54, 1D44(1992).

97. A.Shigeki, S. Tyo, F.Kazuhito and E.Masatoshi, Anal. Chim. Acta, 274, 141 (1993); A.A, 55, 12D14 (1993).

98. S.Abe, K.Fujii and T. Sone, Anal Chim. Acta, 293, 325 (1994); A.A.,57, 1D12 (1995).

99. Z.Cimerman, N. Galic and B. Bosner, Anal. Chim. Acta, 343, 145 (1997); A.A.,59, 9D128 (1997).

100. A Tong, Y. Akama and S. Tanaka , Chem. Express, 5, 285 (1990); A.A, 54, 1D47 (1992).

101. G.J.Goetz-Grandmont, I. Guiguemde, B.A.Diantouba, D. Lakkis and J.P. Brunette, Analusis,24,318 (1996); A.A., 59, 5D38 (1997).

102. E.M. Donaldson and M Wang ,Talanta, 33, 233 (1985); A.A, 48, 7B16 (1986)

103. A.M.Aziz-Alrahman, Int. J. Environ.Anal. chem, 22, 251 (1985);A.A, 48,8F51 (1986).

104. K.V.S. Murty, P.Rama Devi and G.R.K.Naidu, Indian J. chem., Sect.A, 33A, 180 (1994),A.A., 56,9D13 (1994).