

**USE OF A SURFACTANT IN  
THE SPECTROPHOTOMETRY  
DETERMINATION OF TRACE  
AMOUNTS OF NICKEL.**

*A Thesis presented to the  
Ahmadu Bello University*

*in*

*Partial fulfilment for the degree of  
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*ANALYTICAL CHEMISTRY*

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## A C K N O W L E D G E M E N T .

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## A B S T R A C T

The procedure used in establishing a sensitive spectrophotometric method for the determination of nickel in trace level is described.

The method involves the use of a long chain quaternary ammonium salt, cetyltrimethylammonium bromide as a surfactant and Xylenol orange as an indicator.

To arrive at the method, first the optimum conditions for the interaction between the cetyltrimethylammonium bromide (CTAB), xylenol orange (XO) and metal ions were established.

Then the nickel complex Ni-XO-CTAB was chosen for further study.

The conditions for the increased absorbance of the nickel complex were established by observing the U.V. absorbance of the complex.

The results show that the Xylenol orange (XO) and cetyltrimethylammonium bromide (CTAB) interact at pH 10.5 to form stable systems having XO:CTAB mole ratios of 1:2 and 1:6.

The formulae of the systems should be  $[xO \{CTAB\}_2]_n$

and  $[XO(CTAB)_6]_n$  where n is an interger.

The nickel complex was found to have a maximum absorbance at 622 nm with a molar extinction coefficient of  $6.14 \times 10^4 \text{ l. mole}^{-1} \text{ cm}^{-1}$ .

The composition of the nickel complex was studied using the mole ratio method. The mole ratio of Ni:XO in the complex was found to be 1:4.

The formula of the nickel complex should then be Ni  $[\text{XO}(\text{CTABT})_2]_4$  and Ni  $[\text{XO}(\text{CTAB})_6]_4$  for the two established XO:CTAB systems.

The selectivity of the method was studied by observing the absorbance of nickel complex of known concentration of nickel in pure nickel solution and in the presence of some other metal ions.

This study reveals that the selectivity of the method is limited due to interference from iron, cadmium and cobalt ions.

No attempt was made in this study to mask the interfering ions.

## CERTIFICATION

*I hereby certify that this work was carried out by Miss T.A. Abii in the Department of Chemistry, Ahmadu Bello University, Zaria.*

---

DR. J.Y. OLAYEMI  
(Supervisor)

## CHAPTER I

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## INTRODUCTION

Various standard methods have been established for the determination of metallic elements especially in bulk level. Among the established methods are:

- (i) Gravimetric method of analysis
- (ii) Titrimetric method of analysis and
- (iii) Spectrophotometric analysis

### 1.1. Gravimetric Analysis

Gravimetric analysis, usually called quantitative analysis by weight, involves the isolation and weighing of an element or a compound of the element in its pure form.

The element or its compound is separated from a known weight of the substance under study.

Most gravimetric determinations involve the transformation of the element or radical to be determined into a pure compound which can be readily converted into a form suitable for weighing.

The pure compound can then be separated out in a number of ways including (i) Precipitation method and (ii) Electroanalytical method.

1.1.1 Precipitation Method of Analysis

In this method of analysis, the element to be determined is precipitated out of a solution in an insoluble form. The precipitate is then separated out by filtration, washed and dried to a constant weight. Thus in the determination of nickel, a solution of the substance under examination is treated with excess of salicyladehydroxime reagent in very faintly acidic medium.

The precipitate is washed with cold water, dried at 100°C and weighed as dimethylglyoximate<sup>1</sup> of the metal.

Often the element to be determined using this method, and precipitated, is weighed in a form other than that in which it was precipitated. Thus in the determination of magnesium, the element is precipitated as ammonium magnesium phosphate but is weighed after drying as a pyrophosphate<sup>2</sup>.

For a precipitation method of analysis to be successful; the following conditions have been found necessary to be fulfilled:-

- (i) Precipitation processes must be carried out in dilute solutions
- (ii) The precipitate must be sufficiently compact and dense that it can be easily separated from solution by filtration and can be washed free of soluble impurities.
- (iii) The precipitate must be so insoluble that when it is collected by filtration and washed, the loss incurred is very negligible.

In precipitation method of analysis involving trace metal determinations, organic precipitants are usually employed. The precipitants have fairly high molecular weights so that the complex formed with a trace metal ion is consequently of high molecular weight. This property makes the weighings involved in trace metal ion determination more feasible, thus minimising error.

The precipitation method of analysis is however lengthy. It also does not afford the determination of elements to a satisfactory trace level. For example using dimethylglyoximate, not below about 750 ppm nickel can be estimated.<sup>1</sup>

#### 1.2. Titrimetric Analysis

This technique of chemical analysis involves determination of the volume of a solution of accurately known concentration, called standard solution, that is required to react quantitatively with a solution of the substance to be determined.

The weight of the substance is then calculated from the volume of the standard solution used for the reaction and the known law of stoichiometry. The process of adding the standard solution is termed titration. The point at which the titration is complete is called the equivalence point or the theoretical end point.

### 1.2.1 Titrimetric Analysis using visual Indicator

In this method of titrimetric analysis, the end-point is detected by the use of indicators eg. methyl orange, potassium permanganate. These are able to give a clear visual change in the colour of the solution being titrated after the reaction between the standard solution and the solution of the substance being determined is practically complete.

Dyestuffs which form specific complexes with some metals also serve as indicators e.g. murexide and xylenol orange.

The indicators form complexes with metallic ions such as those of nickel, copper, iron, cobalt and many others. The colour contrast between the indicator and the metal indicator complex is such as to be readily observed. The detailed procedure involved is available in some standard text books in chemical analysis.

### 1.2.2. Titrimetric Analysis without Visual Indicator

When there is no visual indicator available for the detection of the end point a method which does not involve a visual indicator is employed. For example (i) the change in the electrical conductivity of the solution can be followed in conductometric titration.

(ii) The change in the absorbance of the solution can be followed during a spectrophotometric titration.

### 1.2.2.1 Conductometric Titration

The principle underlying this method is that ions of one conductivity are substituted by ions of another conductivity. During the course of titration, the conductance of the solution changes. The conductance increases when there is no ionic reaction taking place, as in the addition of one simple salt to the other. When however there is an ionic reaction during titration the conductance either rises or falls. During titration, the conductance is measured after each addition of a volume of the standard solution. The conductance values obtained are plotted against the concentration of the added species to give a graph which consists of two straight lines that intersect at the equivalence point. The accuracy of the method<sup>3</sup> is about (0.5%) and therefore its estimation of trace level of a few ppm is highly limited. The relevant methodology is in many practical analytical Chemistry books 4 - 6.

### 1.2.2.2. Spectrophotometric Titrations

This method involves measuring the absorbance of the solution during titration. The absorbance should follow Beer Lambert's law, i.e. the absorbance should be directly proportional to the concentration of the species absorbing in the solution.

Any addition of the standard solution to the experimental solution produces a change in the concentration of the experimental solution or the absorbing specie and therefore a change in absorbance.

Thus the absorbance of the solution is measured after each addition of a volume of the standard solution.

A plot of the absorbance against volume of standard solution added should give two straight lines that intersect at the equivalence point if a new well defined compound is formed. The accuracy of the method is about a few tenths per cent<sup>7</sup> and therefore cannot satisfactorily estimate trace metals of about a few ppm.

Nevertheless this method has been known to be promising for the estimation of trace metals when some reagents which are known to improve the sensitivity of the measurements are employed. This method has therefore been given a bigger space in the next section.

### 1.3. Spectrophotometric Method of Analysis

Spectrophotometric analysis determines the concentration of a substance by measurement of the relative absorption of light with respect to a known concentration of a substance. A spectrophotometer is often used. The method provides a reliable means for determining minute quantities of a substance.

In recent time ternary complexes wherein a central ion reacts with two different ligands have been employed in the spectrophotometric determination of trace amounts of substance. Papers and reports on this subject are increasing in number. Some of these are those of Fogg et al,<sup>8</sup> Bakko<sup>9</sup>, Burns<sup>10</sup> and Philipanko<sup>11</sup>.

An aspect of this method which is most important in the analysis of substances in trace amounts is the sensitivity which may be obtained from a colour reaction. There are two limitations that govern this. One is instrumental and the other is reagent limitations.

### 1.3.1. Instrumental Limit

The intensity of absorbance (A) of a solution is related to the concentration (c) of the absorbing specie in solution by the Beer-Lambert's Law which is written as

$$A = \log_{10} I_0/I_t = LCE.$$

where  $I_0$  = Intensity of the incident light beam to the solution

$I_t$  = Intensity of the transmitted light beam

L = Path length of the beam in cm

E = Molar Extinction coefficient or Molar Absorptivity.

From the above law, it can be seen that (A) approaches zero logarithmically as  $I_t$  tends to  $I_0$ .

In spectrophotometers, the greatest discrimination is  $\Delta A = 0.002$  absorbance unit. This implies that the difference in the absorbance of two solutions of different concentrations could not be less than 0.002 of an absorbance unit before any meaningful measurement can be made.

This constraint is referred to as instrumental limitation.

### 1.3.2 Reagent Limitation

Sensitivity now depends on the molar absorptivity  $\epsilon$ .

The greater the molar absorptivity, the greater the difference between  $I_0$  and  $I_t$  for a particular concentration of the specie. On the basis of mechanism giving rise to colour, coloured complexes can be divided into three groups.

(i) A complex whose colour is due to a charge transfer between a cation and a ligand e.g. copper I " $\rightarrow$ " neocuprion where the colour is dependent on the process  $\text{Cu (I)} \xrightarrow{h\nu} \text{Cu (II)}$

This type of complex is not common. The colour of the charge transfer complex is quite intense and is characteristic of the particular cation and ligand involved.

(ii) The second type of complex gets its colour from a d-d transition in the cation itself, e.g. manganese salts. This d - d transition is spin forbidden and the colour is not intense and so not useful in spectrophotometry.

(iii) The third type of colour complex and possibly the most relevant to spectrophotometry is that in which a cation or anion complexes with a chromophoric ligand.



This chromophoric ligand is usually an organic molecule of high molecular weight.

The absorbance of the complex depends on the absorbance of the ligand. The observed wavelength of absorption depends on the degree of conjugation in the system. The molar absorptivity of the complex is determined by that of the ligand which has a maximum value of  $10^5$  calculated by Braude<sup>12</sup>.

This maximum value of E imposes the second limitation and is very crucial to the sensitivity of spectrophotometric procedures which depend on the reactions with organic ligands.

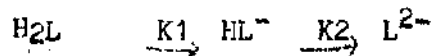
For where these organic ligands constitute the chromophore E will have a maximum value of  $10^5$ .

There are also some other constraints imposed by the reagents.

The technique in spectrophotometry is to add to a trace inorganic ion in solution, an organic molecule which reacts with it to produce a compound that absorbs with spectral characteristics different from either that of the ion or the ligand. This is possible since the presence of the ion will affect the resonance structure of the ligand. This in turn will affect the electronic spacing of the molecular orbitals of the ligand so that different light quanta are necessary for excitation.

Now most metallochromic organic reagents are chelating agents.

They possess ionizable protons which dissociate to produce different absorbing specie e.g.



In a binary complex, the cation  $M^{2+}$  reacts with the chelating agent as



The absorption spectrum of the complex is different from that of the pure ligand but resembles that of the next higher ionization specie of the ligand i.e.  $L^{2-}$  in the above example.

This makes it possible for different suitable cations to react with a ligand and produce similar spectral characteristics.

With ternary complex, the mechanism is quite complicated. The absorption spectrum of the complex formed is also different from those of the reagents but similar to those of the ligand at higher pH. This makes it possible for different ternary metallic complexes to have similar spectral characteristics.

These create the problem of selectivity in spectrophotometric reactions.

However with a ternary complex at lower pH, selectivity can be enhanced.

#### 1.4. Short Comings of Conventional Methods of Analysis

An ideal analytical method would enable a specie to be determined directly in various matrices. Few if any of the above mentioned analytical procedures are wholly specific for a single specie so that the major problem in quantitative analysis is elimination of interference. In Practice the aim of an elimination procedure is to lower

the concentration of the interference to a tolerable level.

While doing this, precautions are taken to ensure that losses of the desired constituents are smaller than the error allowed in the analysis.

In trace determination where the desired trace element is only about 1ppm of the major component, all the above discussed methods have great limitations. They are usually found to be experimentally inadequate in determining a trace element in a sample.

Hence analytical chemists have concerned themselves with increasing the sensitivity of the existing methods and developing more sensitive ones. While doing these, many problems have always surfaced.

Typical among these problems are:

- (i) Insolubility of some of the required analytical reagents and reaction mixtures.
- (ii) Slowness of the reaction upon which the analytical investigations are based.
- (iii) Presence of undesirable side reactions
- (iv) Lack of sufficient sensitivity of the method (v) Interferences and (vi) Instability of the species formed upon which the analytical method is based.

The analytical chemist had in the past either abandoned the development of the potential procedures or restored to using

different systems usually solvents in an attempt to overcome at least some of the above mentioned problems. Only partial success has been reported however.

In recent time, the trend has been to employ surfactants (surface active agents) to minimise some of the above problems.

### 1.5. Surfactants

Surfactants are amphiphilic molecules with a hydrophobic (or non-polar) tail joined to a hydrophilic (or a polar) head group. They are surface active agents that find wide applications in emulsification, wetting, corrosion inhibiting, floatation, foaming and antifoaming.

Surfactants are classified under four headings:-

- (i) Cationic surfactants: These ionize in solution with the head-group carrying a positive charge
- (ii) Anionic surfactants: These ionize with the head-group bearing a negative charge
- (iii) Non-ionic Surfactants, These do not ionize in Solution.
- (iv) Amphoteric surfactants: Which ionize in solution with the head-group carrying a positive or negative charge depending on the pH of the solution

The present study is concerned with the cationic surfactants.

### 1.5.1 Cationic Surfactants

These are divided into two groups. The first group consists of long chain primary, secondary and tertiary amines. They are water soluble only in acidic solution where they ionize to long chain cation and a simple salt anion<sup>13</sup>. The other group consists of quaternary ammonium compounds. These ionize at all pH values to form long chain cations. They can be prepared by quaternizing a tertiary amine with an alkyl halide<sup>13</sup>.

Table I shows some of the cationic surfactants used in analytical chemistry. They include the alkyl-pyridinium salts.

	<u>Name of Surfactant</u>	<u>Common Name</u>
1.	Tetradecyl dimethyl-benzylammonium chloride	Zephiramine
2.	Cetyltrimethyl-ammonium chloride	CTAC
3.	Hydroxy dodecyl trimethyl-ammonium bromide	D.T.M.
4.	Cetylpridinium Bromide	CPB
5.	Cetyltrimethyl-ammonium Bromide	CTAB

Table I: Some common Cationic Surfactants

### 1.5.2. Properties of Surfactants:

Above a certain critical concentrations in aqueous solution, surfactants dynamically associate to form large molecular aggregates of colloidal dimensions termed micelles<sup>14</sup>.

The CMC: Over a narrow concentration range surfactants exhibit an abrupt change in their physical characteristics. This rapid change in properties is known to be generally due to the formation of micelles. The concentration of the surfactant at which this change in physical properties becomes noticeable is called the critical micelle concentration (C.M.C.) Table II gives the values of C.M.C. of some surfactants.

Surfactants	C.M.C.
1. Doecyl dimethyl benzyl-ammonium <sup>15</sup> chloride	$2.8 \times 10^{-3} \text{M}$
2. Tetradecyl dimethyl-benzyl ammonium <sup>15</sup> chloride	$3.7 \times 10^{-4} \text{M}$
3. Hexadecyl dimethyl benzyl ammonium <sup>15</sup> chloride	$4.4 \times 10^{-5} \text{M}$
4. Cetyltrimethylammonium bromide <sup>16</sup>	$6 \times 10^{-6}$

Table II: C.M.C. of some surfactants

At concentrations below the C.M.C., surfactants exist mostly as monomers and behave nearly as simple electrolytes. Above the C.M.C., there exists a dynamic equilibrium between the monomers and micelles.

Each micelle is composed of a certain number of surfactant molecules called aggregation number. This number dictates the size and geometry of the particular micellar system. The orientation is such that, the hydrophilic heads are directed towards and in contact with aqueous medium thus forming a polar surface while the hydrophobic tails are directed away from the water forming a central non-polar core.

### 1.5.3 Structure and shape of micelle.

Although the existence of micelles has been generally accepted, there is disagreement as to their structure and shape.

Debye and Anacker<sup>17</sup> proposed a rod like micelle having a general shape of a stack of coins. This model was derived from a symmetry studies and is in agreement with light

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Debye and Anacker<sup>17</sup> proposed a rod like micelle having a general shape of a stack of coins. This model was derived from a symmetry studies and is in agreement with light scattering data. Hartley<sup>18</sup> proposed the spherical model. He claims that micelles are liquids and so are essentially spherical with their interior approximating the random distribution state



of liquid paraffins but with the hydrophilic end of the ion constrained at the surface of the micelle.

McBian<sup>19</sup> assumed two types of micelle. The first is a spherical ionic micelle of not more than ten like ions. They exist in dilute solutions of surfactants before the CMC is reached.

The second type with little or non-ionic charge is formed just before the CMC so that the solution contains both highly conducting and practically non-conducting micelles. This type he described as lamella micelles composed of alternate layers of water and amphipathic molecules. The molecule layers consist of paraffin chain arranged parallel to each other in liquid rather than crystalline packing.

#### 1.5.4. Solubilization by Surfactants

Solubilization is defined as the spontaneous passage of solute molecules of a substance insoluble in water into an aqueous solution by surfactant in which a thermodynamically stable solution is formed. This involves the diffusion of the molecules of the insoluble solute into the surfactant micelles. Three types of mechanism have been proposed for solubilization phenomenon<sup>19</sup>. The first assumes the absorption of the insoluble solute molecule by the micelles usually on or near the surfactant - water interface.

The second advocates the incorporation of the solute molecules into the hydrocarbon centre of the micelle and the last says the solute molecules penetrate into the polyside layer of the micelle.

#### 1.6. Surfactants in trace Metal Analysis

In recent time, the use of surfactants as micellar systems has been the subject of many studies <sup>20-24</sup> as a potential alternative in an attempt to overcome some of the problems encountered in spectrophotometric methods of analysis of metals especially in trace amounts

Surfactants have been successfully employed in this respect because:-

- (i) Surfactants can form ternary complexes with metal ions and chelometric indicators or dyes. These ternary complexes are known to be more sensitive in spectrophotometric analysis than the conventional binary complex of metal and chelometric indicators.
- (ii) Surfactants have very high solubilizing power and can solubilize a wide variety of solutes otherwise insoluble or sparingly soluble in the bulk solvent.
- (iii) The micellar systems of surfactants can alter greatly the microscopic properties and change the effective microenvironment about any solubilized solute.

The addition of a metal ion in submicro amounts to a solution of a micellar solubilized chelometric indicators usually results

in the formation of intensely coloured complexes. The amount of solute solubilized in the process of complex formation is usually directly proportional to the concentration of the surfactant used provided micelle formation has occurred. These complexes are known to have a characteristic of absorbing at  $620 \pm 30$  nm and have very high molar absorption of about  $(5 \text{ to } 20) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ .

In each instance the formation of the ternary complex is dependent on the formation of micelles<sup>23</sup>.

This was established on the ground that no new complex was formed if the surfactant concentration was below the CMC.

#### 1.6.1 Advantages of Ternary complex over binary complex in Spectrophotometric analysis

The use of surfactant ternary complex has greatly improved the sensitivity of the methods for metal ion determination by u.v. spectrophotometry.

The conventional method involves the complexation reaction between the metal and an indicator to form a binary complex. This procedure suffered from some problems. In some instances, the metal chelate formed was water insoluble. Thus the binary complex formed had to be extracted with a suitable solvent before spectrophotometric measurements were taken.

This step is time consuming and also reduces the sensitivity of the method due to dilution. However when a surfactant is added to the aqueous system, it renders the insoluble metal binary complex soluble<sup>27</sup>. This is due to the formation of aqueous micellar system which solubilizes the metal-indicator complex. The use of surfactant eliminates the extraction step. Since only a very small amount of surfactant is needed for solubilization process, the procedure does not demonstrate decrease in the effective sensitivity of the method. One postulate for the high molar absorptivity of ternary complexes is that the introduction of a third constituent into the binary complex increases the effective area of light absorption of the molecule.<sup>28</sup>

Most colour reactions tend to be unselective. This is because the ligand constituting the chromophoric part of the complex will react with any metal of suitable co-ordination geometry to give the same colour change. There can however be a slight variation arising from differences in the co-valency of the bonding.

The use of ternary complexes involving surfactants enhances selectivity. The chances of other metals duplicating a ternary system is less than in a binary system.

Consider metals  $M^a, M^b$ , of similar chemical character reacting with a ligand  $H_2L$  to give complexes  $M^aL, M^bL$ .

As already been pointed out, the absorption characteristics of most metal complexes of a reagent tends to resemble closely the next higher ionization stage of the ligand molecule in its form as an acid. So when a reagent reacts in the form  $HL^-$ , its metal complexes will resemble that of  $L^{2-}$ . This makes it possible for many metals to form similarly coloured complexes with a ligand making selectivity low. When two ligands  $H_2L$  and  $H_2R$  are involved and a complex  $M-L-R$  is formed, the chance of duplicating such ternary system is reduced. This enhances selectivity.

It has also been found that the binary complex procedures in the absence of micelles sometimes showed poor adherence to Beer's Law due to simultaneous formation of two or more complexes between the metal and chelometric indicator<sup>29</sup>.

In the micellar ternary systems, frequently one type of complex is formed between the metal and the chelometric indicator. This often leads to good adherence to Lambert Beer's Law over a reasonable range of concentration of the metal ion.

Under these conditions measurements are often reproducible and reliable.

### 1.7 Nature of the ternary complexes involving surfactants

A very important condition for the formation of a ternary complex is that the concentration of the surfactant must exceed the CMC so that micelles are formed.

Bailey<sup>30</sup> first established that below the CMC of surfactant used, no ternary complex formation was observed. Hartley<sup>21</sup> first noticed that the colour of the chromophoric agent changed with the addition of surfactants. He utilized the fact that the spectral characteristics of the chromophore are modified at the CMC to determine the CMC of the surfactant:

Another condition for the formation of a ternary complex involving two ligands (a chromophore and a surfactant) is that neither of the ligands alone forms a co-ordination saturated complex with the metallic ion. This means that one ligand should not be able to satisfy fully all the co-ordination requirements of the metallic ion so that the second ligand can still take part in the co-ordination reaction.

#### 1.7.1 Stoichiometry of ternary complexes

West et al.<sup>18,23</sup> initiated work on the sensitization of colour reactions involving metal-chelate systems. They worked with and sensitized the Tin (iv) - catechol violet reactions with cetyltrimethylammonium bromide.

By means of photometric titrations and method of continuous variation they have shown that the complex Tin (iv) - Catechol violet - CTAB has the stoichiometry of 1:2:4. This means that the complex has a definite composition. This has been supported by many workers. Wet and Brehens<sup>20</sup> used the same method and established the stoichiometry of 1:2:4 for the complex formed between Xylenol orange, cetylpyridinium bromide (CPB) and the rare earth metals. Apart from being a complex of definite stoichiometry, the interaction between metal, surfactant and dyes can be in a form of ion-associates. This is supported by the work of He XI - Wen et al.<sup>21</sup>

Working with iron III, bromopyrogallol red (BPR) and hexadecyltrimethyl-ammonium bromide (CTMAB), they found that the complex formed contained three molecules of BPR coordinated to an iron III ion and two molecules of CTMAB associated with each BPR molecule giving an overall formula  $(CTMAB)_6(BPR)_3 Fe(III)$ .

## CHAPTER TWO

Preliminary Investigation for optimum conditions  
for the interaction between xylenol orange (XO),  
cetyltrimethylammonium bromide (CTAB) and  
metallic ions

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## CHAPTER TWO

Preliminary Investigation for optimum Conditions  
for the interaction between Xylenol orange (XO),  
cetyltrimethylammonium bromide (CTAB) and  
Metallic ions.

From literature it appears the combination of xylenol orange (XO) and cetyltrimethylammonium bromide (CTAB) in trace metal analysis has not received enough attention.

In the present work, the optimum conditions for the interaction between XO and CTAB is investigated.

Under the worked out conditions the interaction of the complex XO-CTAB with some metal ions was studied by observing their absorbance of the U.V. radiation.

Among the metal ions studied the interaction with nickel was found to be of interest. Hence the complex CTAB - XO - Ni was chosen for further study.

## 2.1. Xylenol Orange Study

### Reagents and solutions

All the chemicals used in this work were of the analytical grade of purity except Xylenol orange which was of the reagent grade. They were all used without further purification.

(i) Xylenol Orange XO (C<sub>31</sub> H<sub>32</sub> N<sub>2</sub> O<sub>13</sub>S) (4x10<sup>-4</sup>M)

0.0269g of xylenol orange was dissolved with distilled deionized water and made up to 100cm<sup>3</sup> in a standard volumetric flask.

(ii) Sodium hydroxide (10<sup>-2</sup>M)

Standard NaOH solution in ampule, was appropriately diluted with distilled deionized water in a standard flask to obtain a 10<sup>-2</sup>M solution.

Apparatus:(i) Spectrophotometer:

All absorbance measurements were made with a Unicam SP 1750 B Spectrophotometer and 10 nm Silica cells.

(ii) pH Meter

pH values were determined with W.G.PYE Model 290 pH meter.

2.1 Potentiometric titration of aqueous xylenol orange solution with sodium hydroxide

Method:

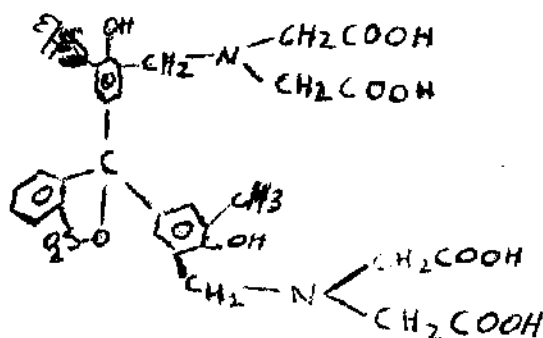
2 cm<sup>3</sup> of the stock xylenol orange (4x10<sup>-4</sup>M) solution was accurately measured into a 50 cm<sup>3</sup> volumetric flask.

0.2 cm<sup>3</sup> of the sodium hydroxide 10<sup>-2</sup>M was added and the solution was made up to the 50cm<sup>3</sup> mark with distilled deionized water. The pH of the solution was found using the pH meter. This was repeated several times with the same concentration of XO but different and increasing volumes of the 10<sup>-2</sup>M sodium hydroxide.

A plot of pH against the volume of sodium hydroxide gives the potentiometric titration curve fig. 2.1.

### Results and discussions

Aqueous xylenol orange solution is essentially acidic as shown by both the initial pH of about 4.2 in water and from the structural formula shown below:



It quickly releases its proton to a base as shown by the steep rise in pH with the addition of NaOH.

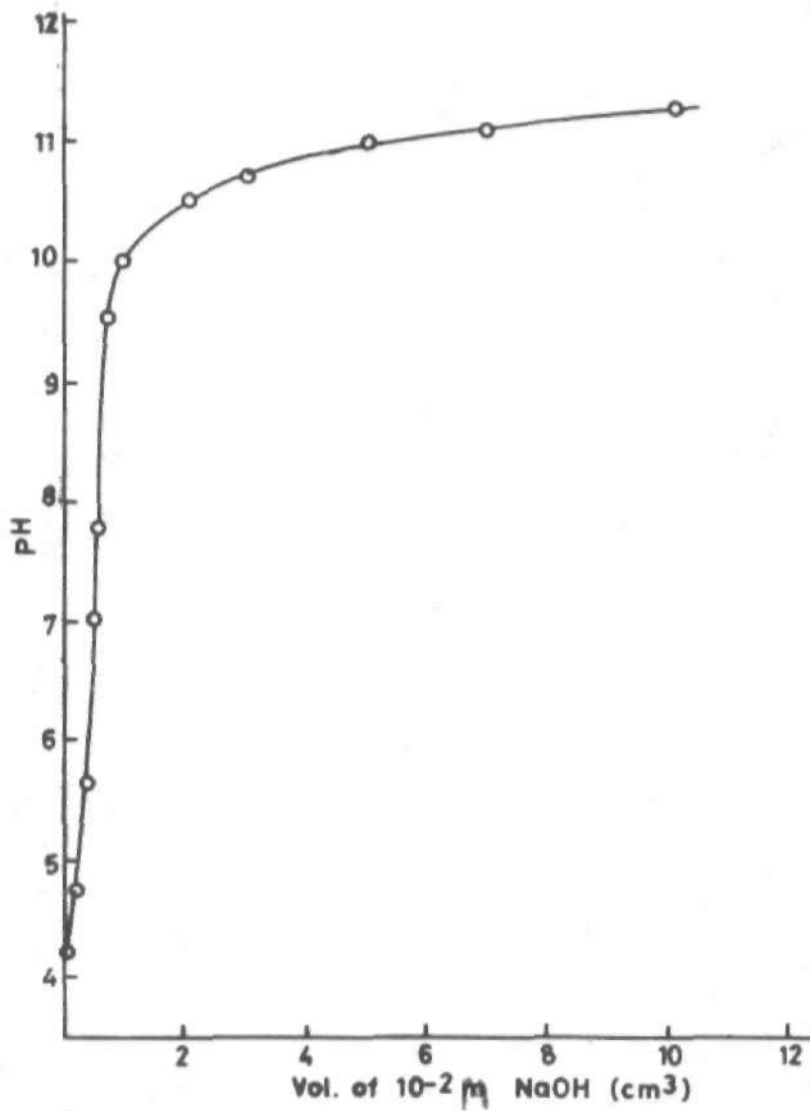


Fig. 2.1 Potentiometric titration of xylenol orange solution with sodium hydroxide.

$$[\text{XO}] = 4 \times 10^{-5} \text{ M}$$

The aqueous solution of xylenol orange appears to be well buffered against pH changes above about pH 10.5, fig.2.1. Hence an aqueous xylenol orange solution at pH 10.5 and above would be anionic when not bound covalently to another group. In the presence of sodium ions, there is expected to be an ionic interaction between the two kinds of ions.

#### 2.1.2. The Dependence of the absorbance of aqueous xylenol orange solution on pH.

##### Method:-

To 3 cm<sup>3</sup> of the 4x10<sup>-4</sup>M XO solution in different 50 cm<sup>3</sup> standard flasks was added sodium hydroxide (10<sup>-2</sup>M) solution. The volumes of sodium hydroxide solution added were selected to give different values of pH of a sufficient spread on finally diluting the xylenol orange solution to the 50cm<sup>3</sup> mark with distilled deionized water.

The U.V. absorption spectrum of each xylenol orange solution was determined using the spectrophotometer and related to the pH of the solution which was measured immediately after the spectrophotometric study.

##### Results

The results are shown in fig 2.2a and fig 2.2b. Fig.2.2a shows only two curves for two of the several pH values investigated, but the absorption maximum was found



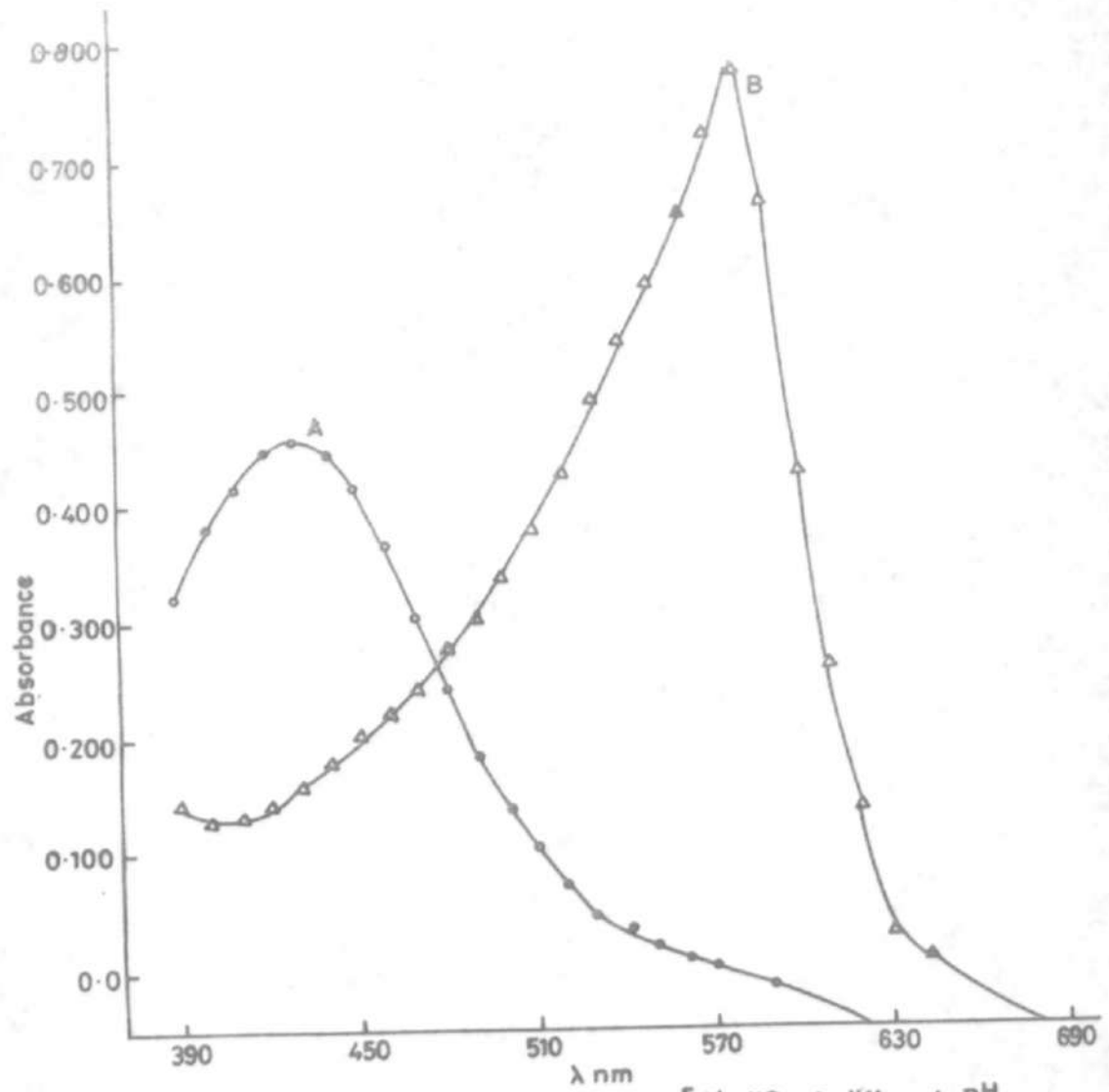


Fig. 2-2a Absorption spectra of  $2.4 \times 10^{-5} M$  XO at different pH  
Curve A at pH 4.4  
Curve B at pH 10.6

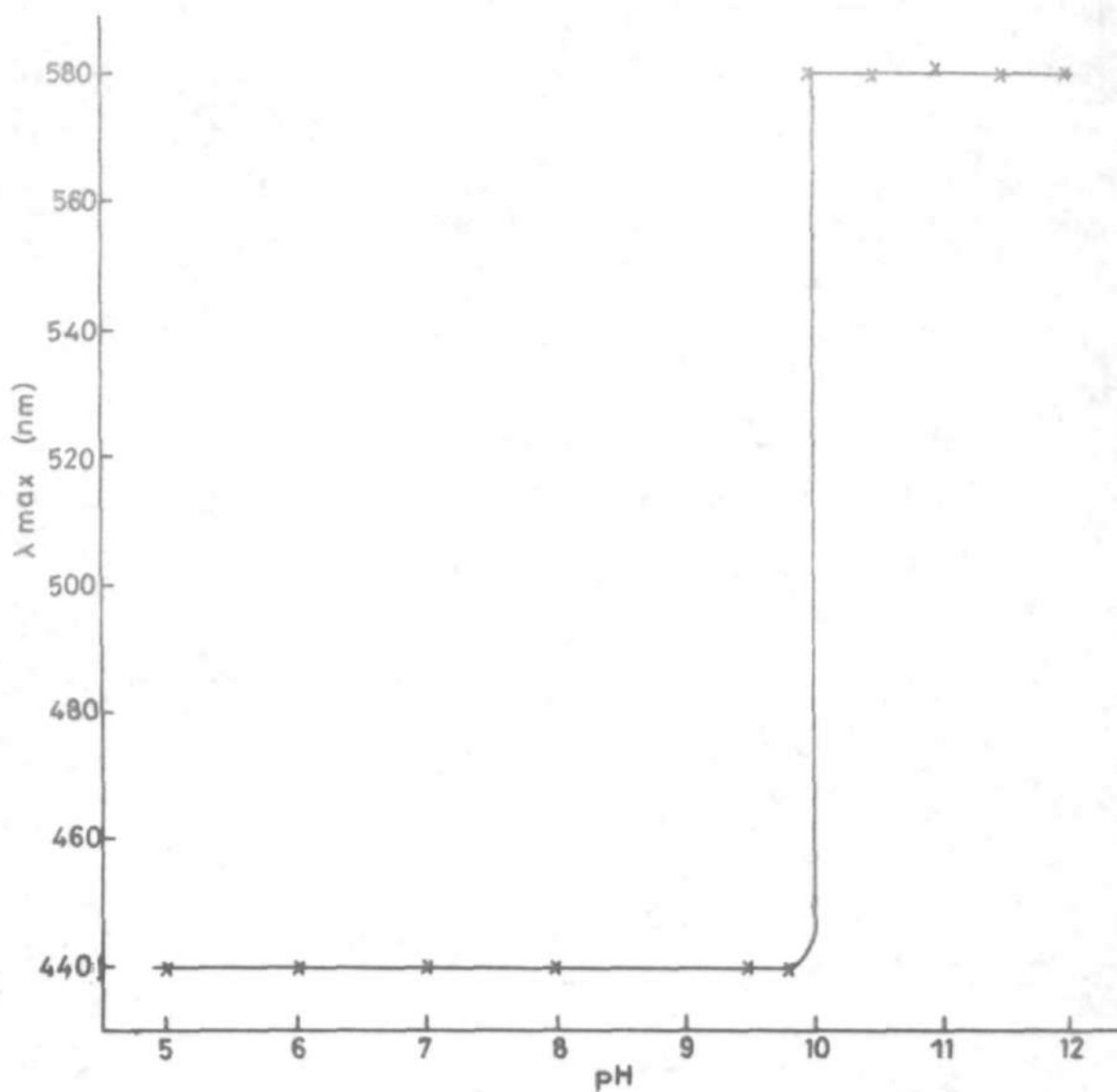


Fig. 2-2b Variation of wavelength of absorption maximum of aqueous solution of  $8 \times 10^{-6} M$  xlenol orange with pH

to depend on pH as indicated by fig. 2.2b, having a value of 440 nm between pH 5 to pH 9.8 and 580 nm above pH 10.

The highly acidic range of the indicator was not studied.

Figs 2.2a and 2.2b agree well with earlier report.<sup>32</sup>

The increase in  $\lambda_{\text{max}}$  of the UV absorption of aqueous solution of XO with pH was very sharp over a very narrow pH range.

This indicates that XO can be made to exist in water in at least two distinct forms with characteristic electron systems.

## 2.2. Determination and maximising the conditions for xylenol orange and cetyltrimethylammonium bromide XO/CTAB interactions.

### 2.2.1 Reagents

#### (i) Xylenol Orange (XO) $4 \times 10^{-4}$ M at pH 10.5

0.269g xylenol orange was dissolved in distilled deionized water. 5 cm<sup>3</sup> of the stock sodium hydroxide ( $10^{-2}$  M) solution was added and the solution made up to the mark with distilled deionized water in a 100 cm<sup>3</sup> standard volumetric flask.

(ii) CTAB ( $4 \times 10^{-4} \text{M}$ )

0.1458g of CTAB was dissolved in a litre standard volumetric flask with distilled deionized water. The solution was made up to the  $1000 \text{ cm}^3$  with same distilled deionized water.

(iii)  $\text{NaHCO}_3/\text{NaOH}$  buffer of pH 10.5

$500 \text{ cm}^3$  of  $5 \times 10^{-2} \text{M}$   $\text{NaHCO}_3$  (4.2g/l)

and  $178 \text{ cm}^3$  of  $0.1 \text{M}$   $\text{NaOH}$  (4g/l)

were mixed together and diluted with distilled deionized water to  $1000 \text{ cm}^3$  in a standard flask.

2.2.1 Methods

(i) Interaction between CTAB and XO

$2 \text{ cm}^3$  aliquots of  $4 \times 10^{-4} \text{M}$  aqueous xylenol orange solution at pH 10.5 were accurately measured into different  $50 \text{ cm}^3$  standard volumetric flasks.

Different volumes of  $4 \times 10^{-4} \text{M}$  CTAB solution were added to each flask and the solution made up to  $50 \text{ cm}^3$  with distilled deionized water.

The wavelength of maximum absorbance and the corresponding absorbance value for each solution were determined using the spectrophotometer. Measurements were made in 10mm cells using distilled deionized water as blank.

## Results

The results are presented graphically in fig 2.3a and fig 2.3b.

Fig 2.3a shows only two of the several curves obtained for xylenol orange solution of the same concentration but different concentrations of CTAB.

The dependence of  $\lambda_{\max}$  for XO/CTAB system on CTAB is described in fig 2.3b. Over the range of the ratio of CTAB/XO investigated,  $\lambda_{\max}$  for the XO-CTAB system had a value of 580nm up to the CTAB/XO molar ratio of 2:1. The value of  $\lambda_{\max}$  increased gradually to a constant value of 592nm at CTAB/XO ratio of 6:1.

The results show a bathochromic shift of 12nm in  $\lambda_{\max}$  of the alkaline xylenol orange solution from 580nm to 592nm.

The purple colour of the alkaline xylenol orange changed to violet blue when the six fold mole excess of CTAB relative to XO was reached.

Accompanying the bathochromic shift in  $\lambda_{\max}$  was a decrease in absorption of the alkaline aqueous xylenol orange solution. This decrease is maximum and constant at about 6:1 molar ratio of CTAB / XO . fig 2.3.a.

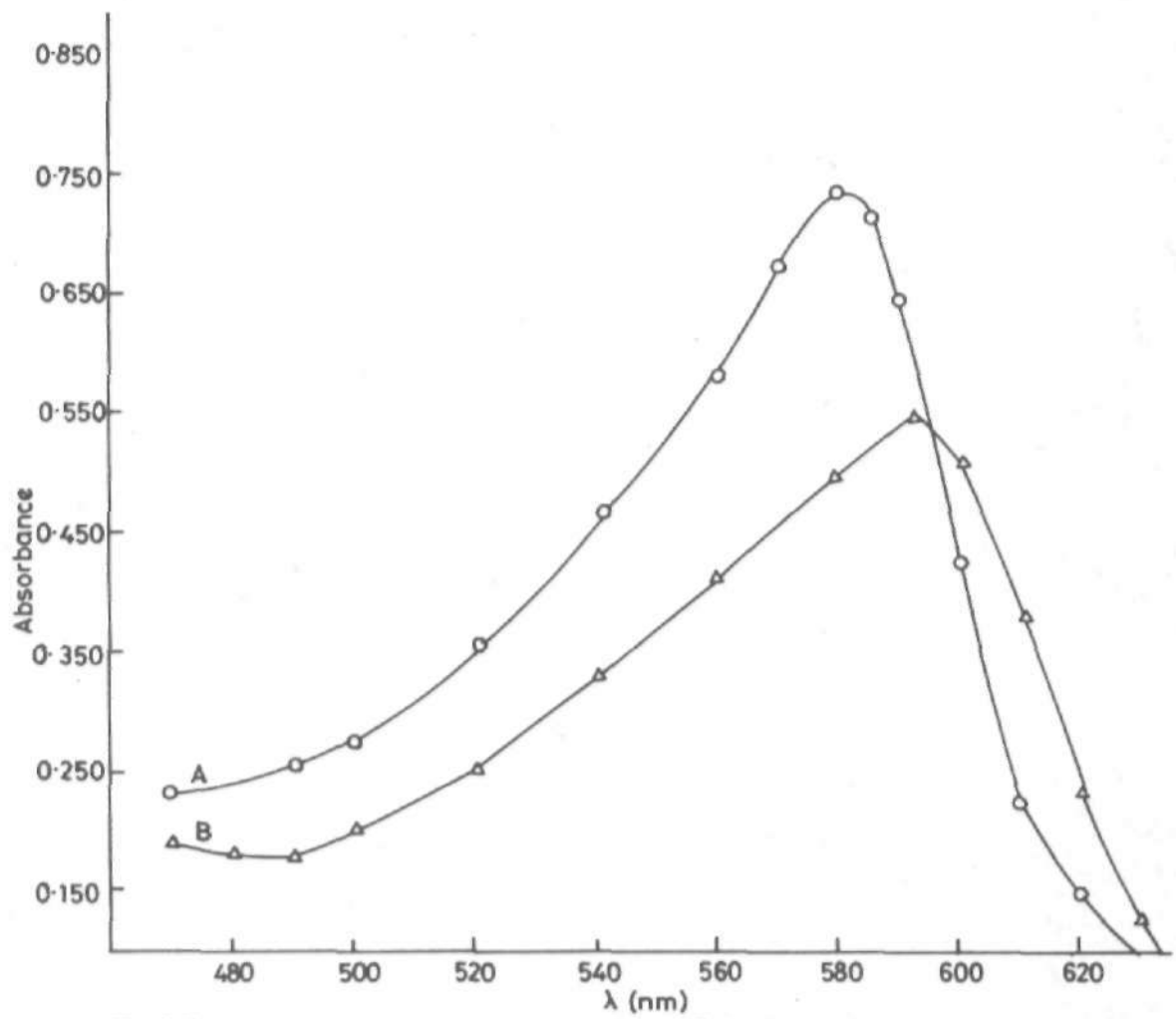


Fig. 2-3a Absorption spectra of XO - CTAB system

A : XO in  $1.28 \times 10^{-5} M$  CTAB /  $1.6 \times 10^{-5} M$  XO

B : XO in  $1.6 \times 10^{-4} M$  CTAB /  $1.6 \times 10^{-5} M$  XO

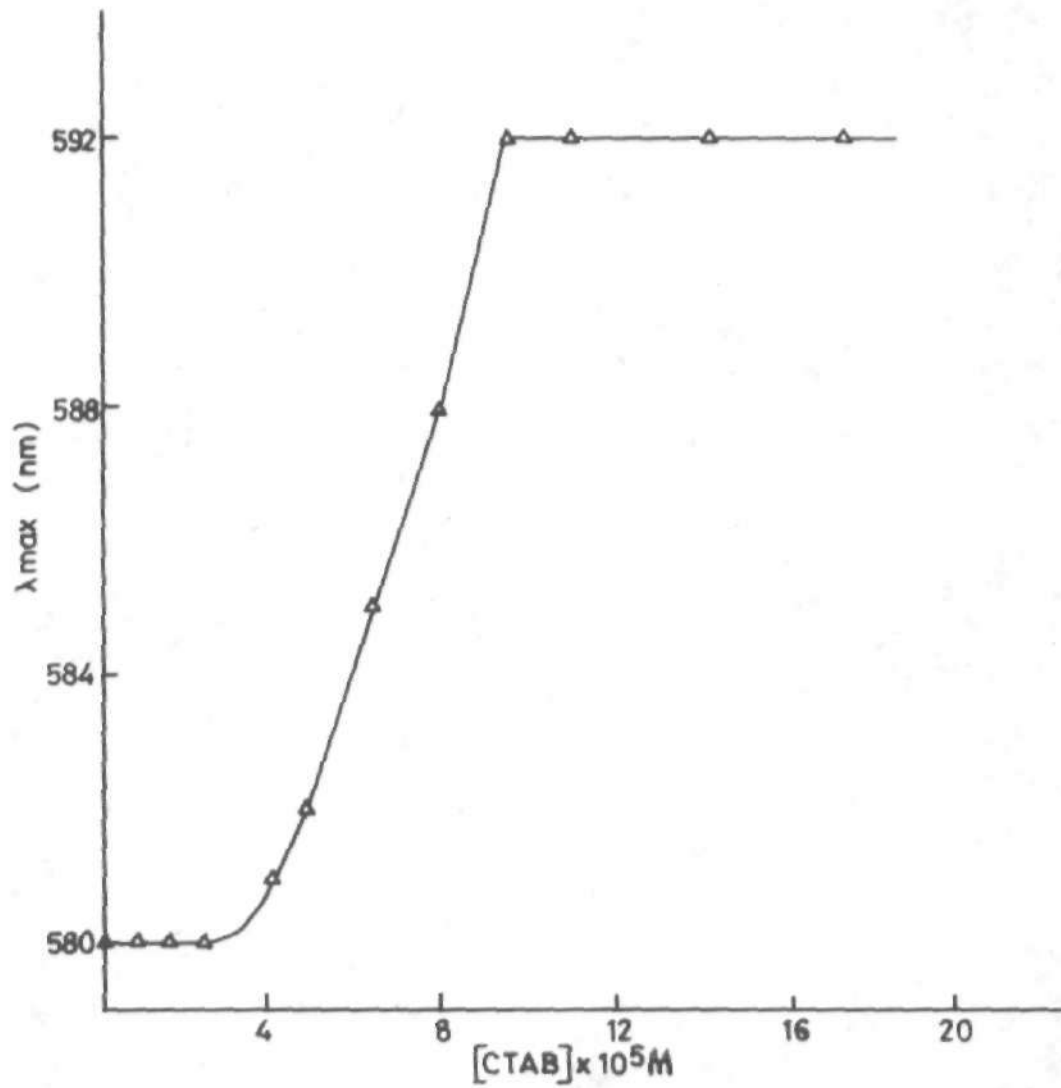


Fig.2-3b Variation of the wavelength of maximum absorption of XO with concentration of CTAB  
[XO] =  $1.6 \times 10^{-5} M$ ; pH 10.5  
Blank = distilled deionized water

(ii) Effect of NaHCO<sub>3</sub>/NaOH buffer of pH 10.5 on the absorbance of the XO - CTAB System

2 cm<sup>3</sup> of 4x10<sup>-4</sup>M XO was accurately measured into a 50 cm<sup>3</sup> standard flask. 20cm<sup>3</sup> of the 4x10<sup>-4</sup>M CTAB was added followed by 10cm<sup>3</sup> of the buffer solution. The solution was made up to the 50 cm<sup>3</sup> mark with distilled deionized water.

Other similar solutions were prepared using the same 2cm<sup>3</sup> of 4x10<sup>-4</sup>M XO and 20 cm<sup>3</sup> of 4x10<sup>-4</sup>M CTAB but different volumes of the buffer solution.

The UV absorbance at 592 nm of each solution was measured with the spectrophotometer using 10mm cells and water as blank.

The pH of each solution was also measured with the pH meter

Results:

Fig 2.4 is the graph of absorbance of the system of 1.6x10<sup>-5</sup>M aqueous XO solution, 1.6x10<sup>-4</sup>M CTAB in buffer solution against the volume of the NaHCO<sub>3</sub>/NaOH buffer solution of pH 10.5 added.



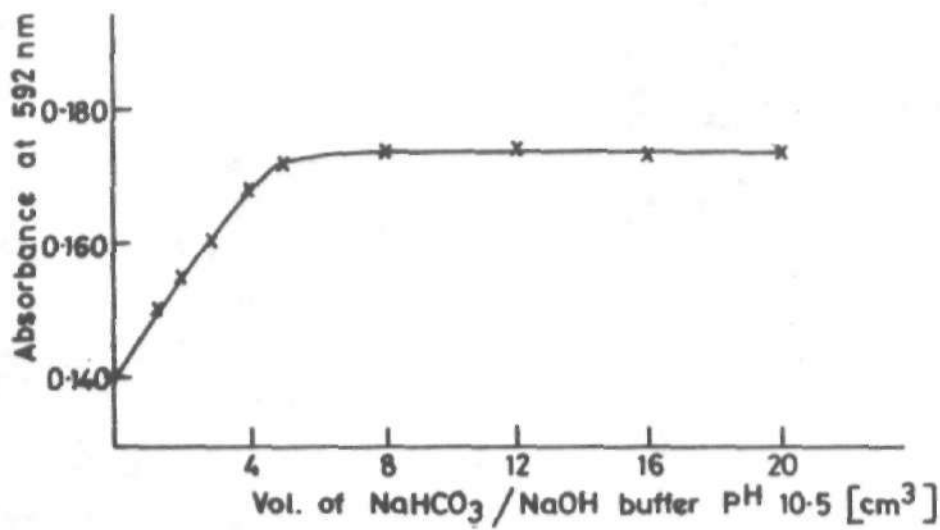


Fig. 2.4 Effect of concentration of buffer on the the absorbance of XO/CTAB complex: Buffer blank:  $[XO] = 1.6 \times 10^{-5} M$ ;  $[CTAB] = 1.6 \times 10^{-4} M$

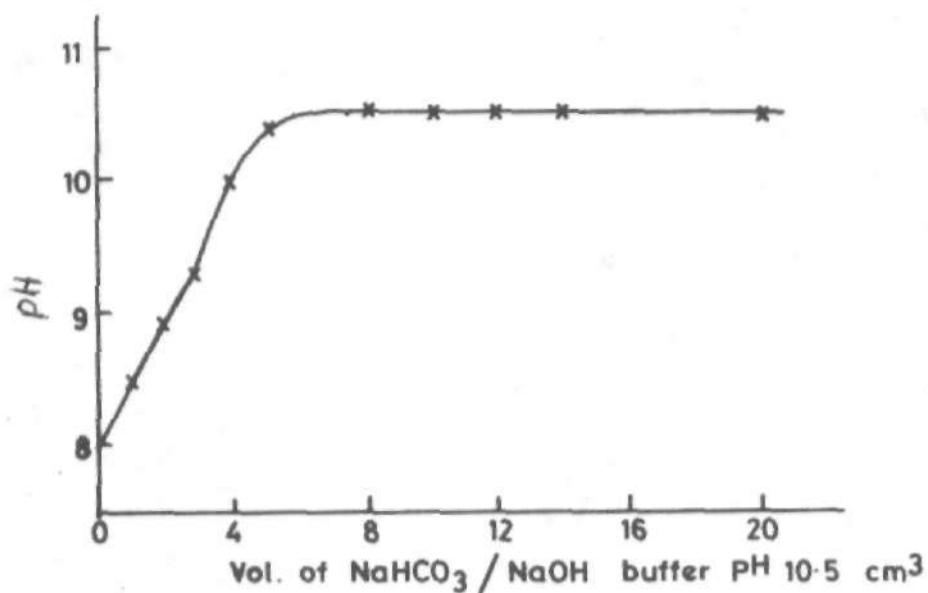


Fig. 2.5 Effect of concentration of buffer on the pH of the XO/CTAB complex.

$$[XO] = 1.6 \times 10^{-5} M; [CTAB] = 1.6 \times 10^{-4} M$$

The results show that the absorbance of the system CTAB-XO at 592nm increased with the increase in the concentration of the  $\text{NaHCO}_3/\text{NaOH}$  buffer pH 10.5 and reached a constant value at about 6  $\text{cm}^3$  of the buffer solution.

Fig 2.5 shows the variation of the pH of the complex CTAB-XO in buffer, with increase in the concentration of the  $\text{NaHCO}_3/\text{NaOH}$  buffer of pH 10.5.

The pH of the solution containing the complex reached pH 10.5 gradually by an increase in the concentration of the buffer. The smallest volume of the  $2.3 \times 10^{-2} \text{M}$   $\text{NaHCO}_3/\text{NaOH}$  buffer required to reach pH 10.5 was 6  $\text{cm}^3$ . The pH of the experimental solution remained at 10.5 as from about 6  $\text{cm}^3$  of the carbonate buffer solution. For all subsequent works, 10 $\text{cm}^3$  of the ( $2.3 \times 10^{-2} \text{M}$ )  $\text{NaHCO}_3/\text{NaOH}$  buffer solution pH 10.5 was used.

2.3. Determination of the molar ratio of XO: CTAB in the complex XO-CTAB

2.3.1 The Effect of the Concentration of XO on the minimum Concentration of CTAB required to produce the maximum bathochromic shift of 12 nm from 580 nm

Method:-

1 cm<sup>3</sup> of the alkaline 4x10<sup>-4</sup> M XO was accurately measured into a 50 cm<sup>3</sup> standard flask and 10 cm<sup>3</sup> of the NaHCO<sub>3</sub> /NaOH buffer solution was added. 1 cm<sup>3</sup> of the 4x10<sup>-4</sup> M CTAB was added and the mixture made up to 50 cm<sup>3</sup> with distilled deionized water. The  $\lambda_{max}$  of the absorption from the solution was measured in the spectrophotometer in 10mm cells using the same concentration of XO and buffer used in the sample as blank. This was repeated using different volumes of CTAB but same volume of XO and buffer as described. The entire steps described above were repeated using 20 cm<sup>3</sup> and 3cm<sup>3</sup> of the XO in turn.

Results:-

The results are presented in fig 2.6. as the dependence of  $\lambda_{max}$  on (CTAB) for three concentrations of xylenol orange.

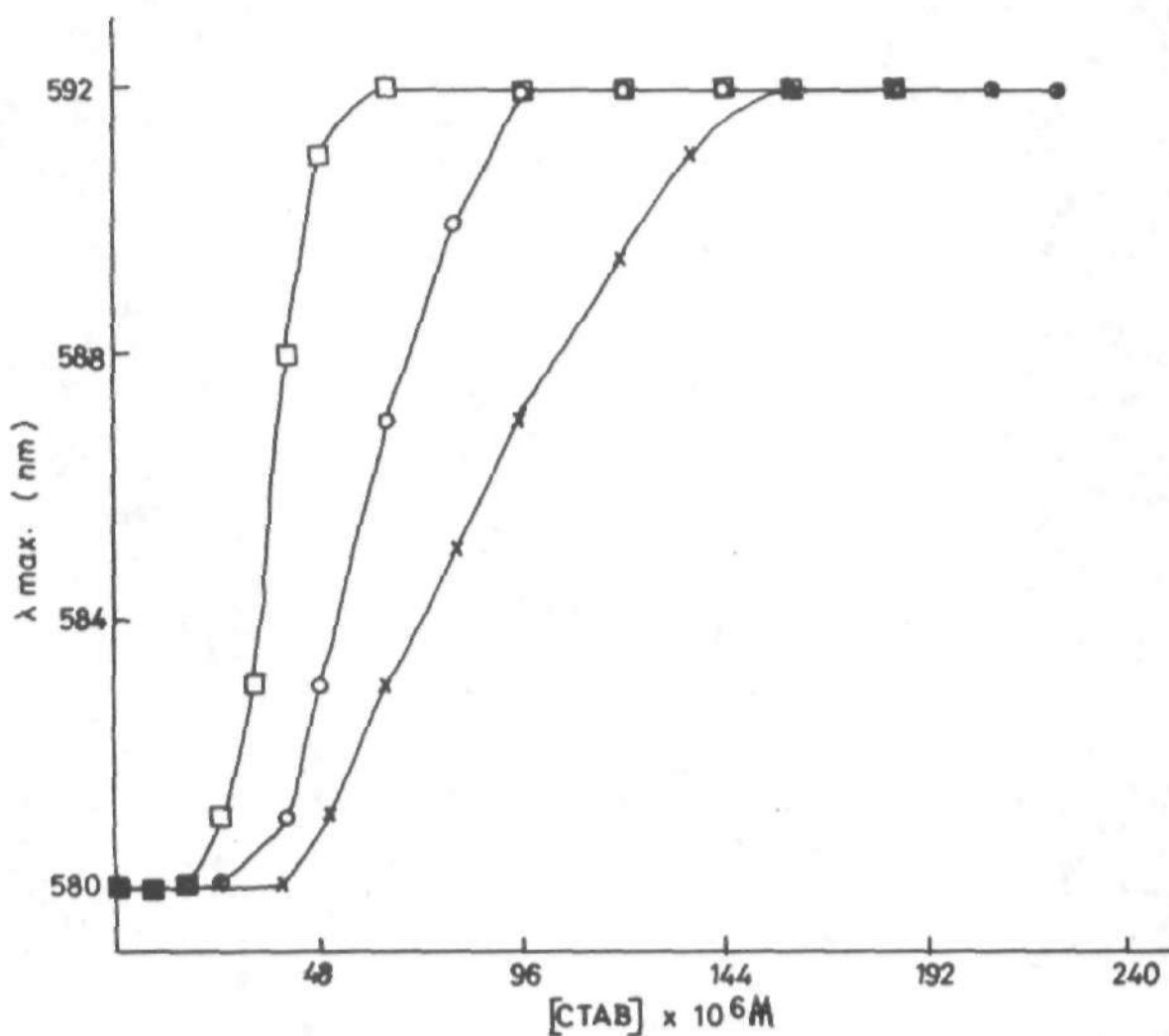


Fig.2-6. Variation of  $\lambda_{max}$  of CTAB-XO with CTAB for different concentrations of XO.

A :  $[XO] = 8 \times 10^{-6} M$

B :  $[XO] = 1.6 \times 10^{-5} M$

C :  $XO = 2.4 \times 10^{-5} M$

These results indicate that the concentration of CTAB needed to cause a bathochromic shift in the absorption of XO from 580 nm to 592 nm was dependent on the concentration of the XO used while the maximum bathochromic shift of 12nm was independent of XO concentration.

For all cases studies, the ratio of  $[XO] : [CTAB]$  to produce maximum bathochromic shift in wavelength is 1:6.

It is interesting to note from the shape of the graphs in fig 2.6 that the change in  $\lambda_{max}$  of absorbance starts immediately after the  $[XO] : [CTAB]$  ratio of 1:2 in all the cases. These results suggest a possibility of two types of complexes, one  $XO (CTAB)_2$  and the other  $XO (CTAB)_6$  depending on the concentration of CTAB.

### 2.3.2 The Effect of CTAB Concentration on:-

- (i) Absorbance at 580nm
- (ii) max absorbance and
- (iii)  $\lambda$  max of XO solution.

#### Method

2cm<sup>3</sup> of the alkaline 4x10<sup>-4</sup>M aqueous XO was accurately measured into a 50cm<sup>3</sup> standard flask.

10cm<sup>3</sup> of the NaHCO<sub>3</sub>/NaOH buffer was added followed by 1cm<sup>3</sup> of 4x10<sup>-4</sup>M CTAB. The solution mixture was made up to 50 cm<sup>3</sup> with distilled deionized water. Using the spectrophotometer, 10nm cell and buffer solution as blank, the following were determined

- (i) Absorbance at 580nm
- (ii) Absorbance at  $\lambda$ max and
- (iii)  $\lambda$ Max

The entire process above was repeated for various concentrations of CTAB but the same concentrations of XO and buffer solutions.

#### Results:-

Fig. 2.7 shows the graph of the various parameters against the concentration of CTAB.

Generally the pattern of variation of these three parameters indicate that two different complexex were formed between XO and CTAB, one at 1:2 of  $[XO] : [CTAB]$  and the other at 1:6 of  $[XO] : [CTAB]$  confirming the results of fig. 2.6.

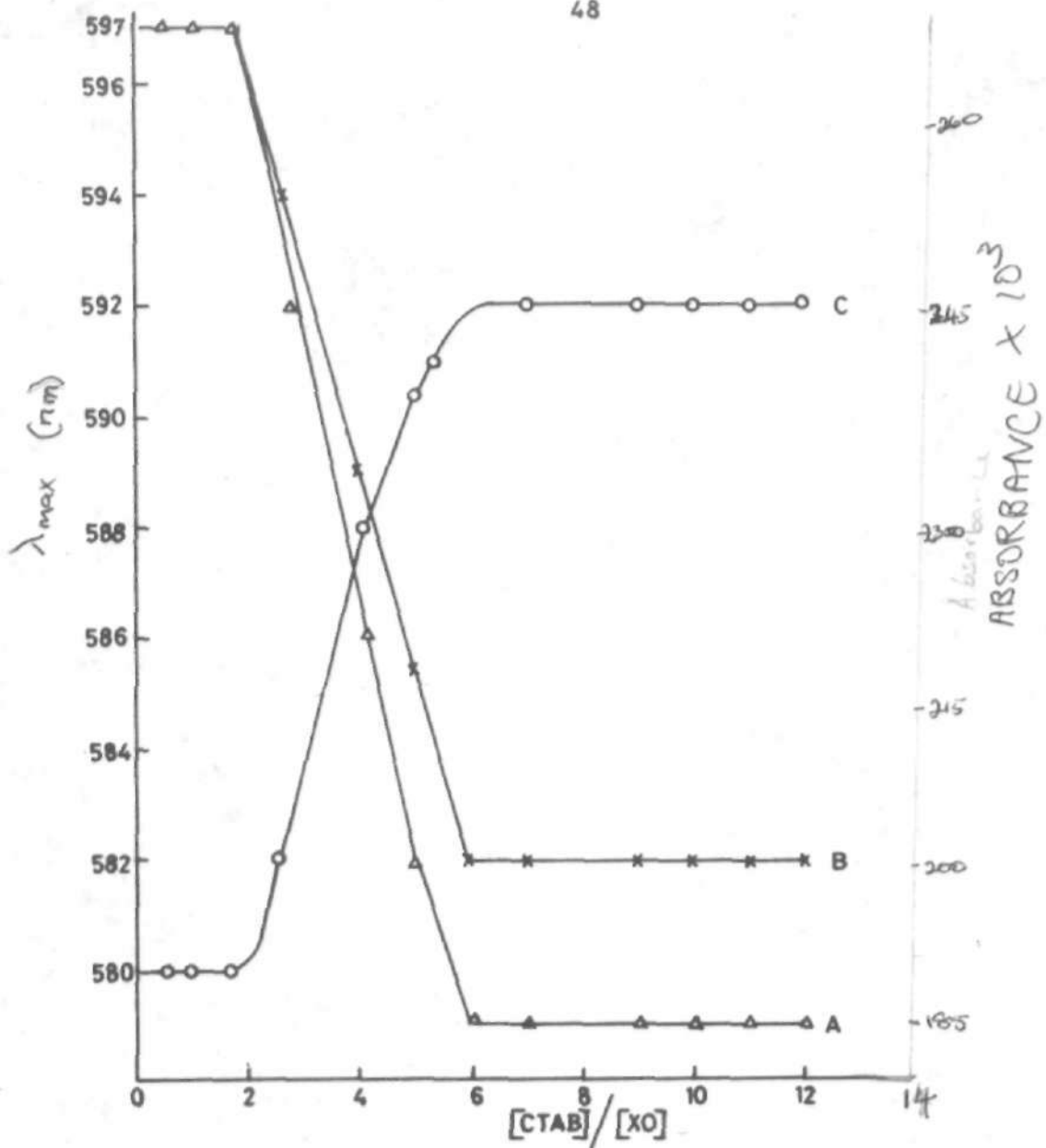


Fig. 2.7. The effect of CTAB conc. on :-  
 A = Absorbance at 580 nm  
 B = " "  $\lambda_{max}$   
 C =  $\lambda_{max}$  of  $[XO]$  of  $1.6 \times 10^{-5} M$

While the absorbance at 580nm and the wavelength of absorption maximum first remained constant up to the point where XO/CTAB is 1:2, and decreased linearly; to a constant value at 1:6 of XO/CTAB, the wavelength of the absorption maximum, ( $\lambda_{max}$ ) first remained constant up to 1:2 of XO/CTAB, increased to a point of 1:6 of XO/CTAB and remained constant.

The concentration of CTAB at which the parameters i.e. Absorbance at 580nm, Absorbance at  $\lambda_{max}$  and  $\lambda_{max}$  are no longer affected by further increase in the concentration of the CTAB must be that at which the most stable complex of XO/CTAB of a specific stoichiometry is formed. This complex from the graphs should have the molecular formula of  $[XO(CTAB)_6]_n$  where  $n$  is an integer and might be unity.

The initial constant values of these parameters respectively suggests the formation of a rather unstable second complex of formula  $XO(CTAB)_2$  at a lower concentration of CTAB.



2.3.2.1. Change of (i) Molar absorptivity of XO at 580nm and (ii) Change in absorbance at the  $\lambda_{max}$  of the XO/CTAB system with addition of varying concentrations of CTAB.

Method:

The experiment was performed as in 2.3.2. From the data on absorbance at 580nm of XO with addition of CTAB, absorptivity of XO on addition of CTAB, was calculated for different concentrations of CTAB. It is plotted against the concentration of CTAB in fig. 2.8. Similarly from the data of Absorbance at  $\lambda_{max}$  the change in absorbance of the XO/CTAB system on addition of CTAB was calculated for different concentrations of CTAB. It is plotted against the concentration of CTAB in fig. 2.9.

The change in absorbance at the  $\lambda_{max}$  of the XO/CTAB complex with addition of CTAB is defined as  $(A_i - A_o) = \Delta A$ , where  $A_i$  is absorbance at  $\lambda_{max}$  of the XO/CTAB complex with concentration of (CTAB)<sub>i</sub> mole l.  $A_o$  is absorbance at  $\lambda_{max}$  of XO at zero concentration of CTAB.  $\Delta A$  is change in absorbance of XO/CTAB complex.

Results:

Figs 2.8 and 2.9 agree well with fig. 2.6 and 2.7. The two parameters first remained constant up to 1:2 ratio of XO /CTAB . Then there was a linear change which became constant at a 1:6 ratio of XO /CTAB .

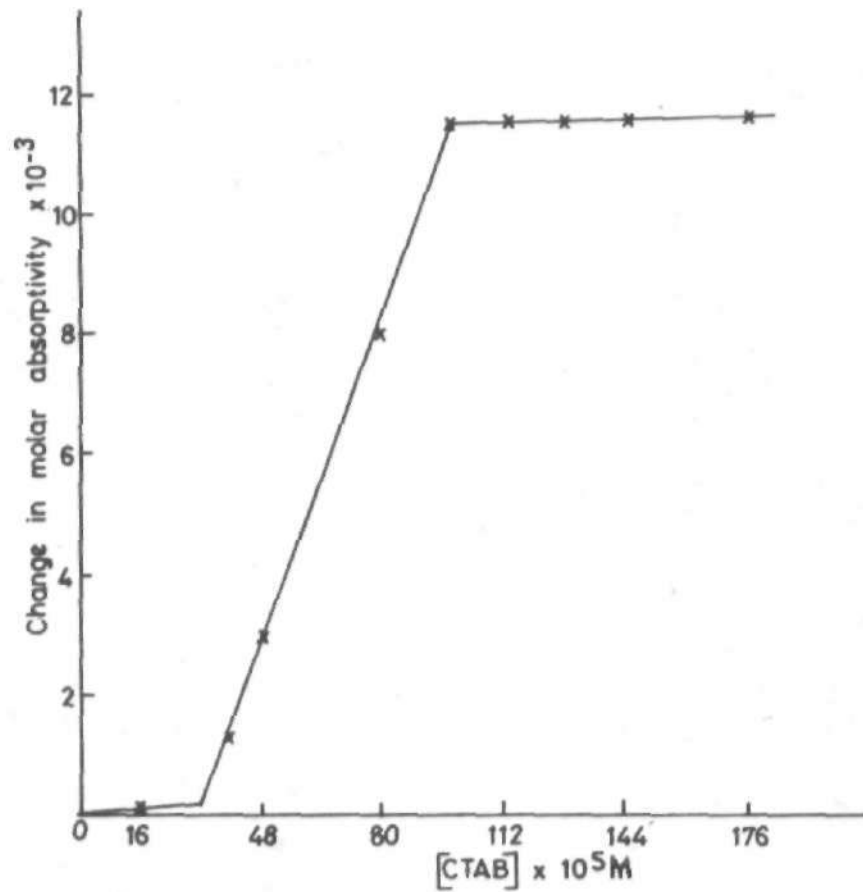


Fig. 2-8 Variations of change in molar absorptivity of XO with [CTAB] at 580 nm  
Con. of [XO =  $1.6 \times 10^{-5} M$ ]

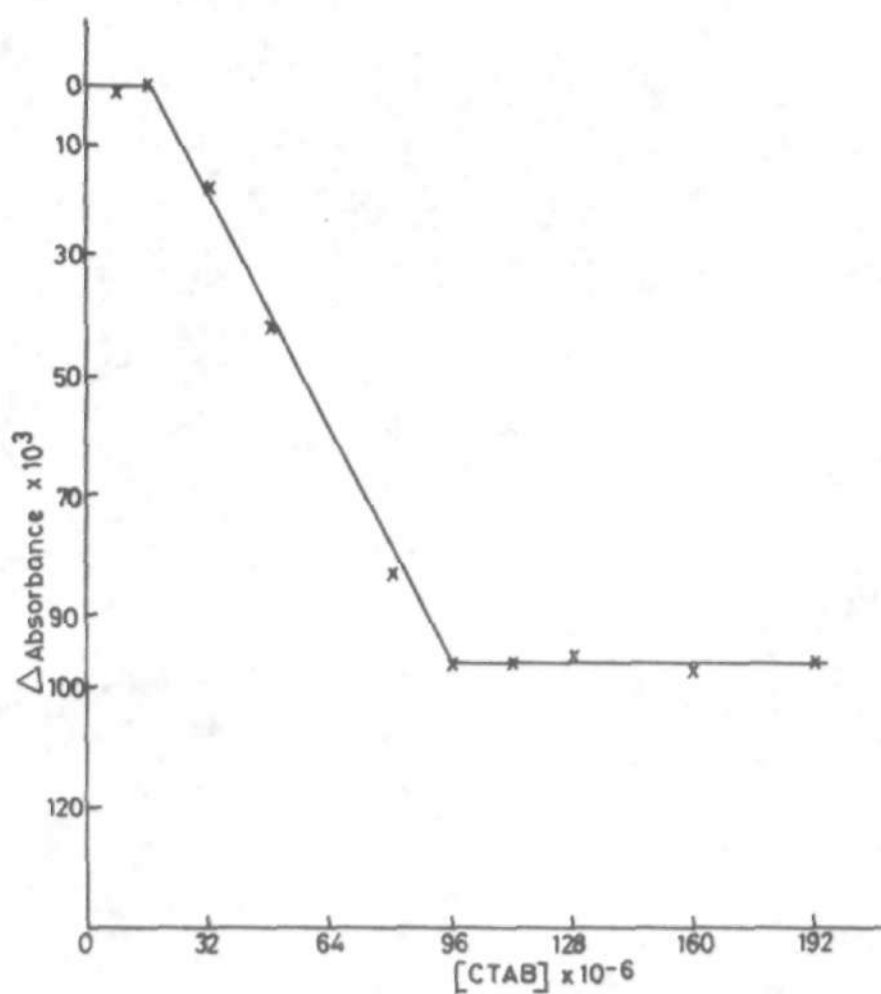


Fig. 2-9. Variation of change in absorbance  $\Delta A$  of XO at 580 nm with CTAB concentration.  
 $[\text{XO}] = 1.6 \times 10^{-5} \text{M}$

These results confirm the two complexes of XO and CTAB with formula  $XO(CTAB)_2$  and  $[XO(CTAB)_6]_n$  obtained in 2.3.1 and 2.3.2.

### 2.3.3. Study on the interaction between XO and CTAB at different pH

This was done by obtaining and comparing the absorption spectra of XO and XO-CTAB systems at different pH values.

Fig 2.10 shows the result.

Curve A is the absorption spectrum of  $2.4 \times 10^{-5} M$  XO at pH 4.2 while curve B shows the effect of  $4 \times 10^{-4} M$  CTAB on the acidic xylenol orange solution.

Curve C is the absorption spectrum of alkaline XO at pH 10.5 while curve D shows the effect of  $4 \times 10^{-4} M$  CTAB on the alkaline XO solution.

### Results and Discussions

The absorption Spectra of xylenol orange solutions at pH 4.2 show a characteristic absorption maximum at 440nm, curve A. After the addition of CTAB, this maximum decreased with a bathochromic shift of about 12nm from 440nm to 428nm. curve B, while a second absorption peak appears at 592nm.

Similarly alkaline xylenol orange at pH 10.5 showed a characteristic absorption maximum at 580nm. Addition of CTAB results in a decrease in this maximum with a bathochromic shift of about 12nm from 580nm to 592nm, while a second absorption peak appears at 440nm.

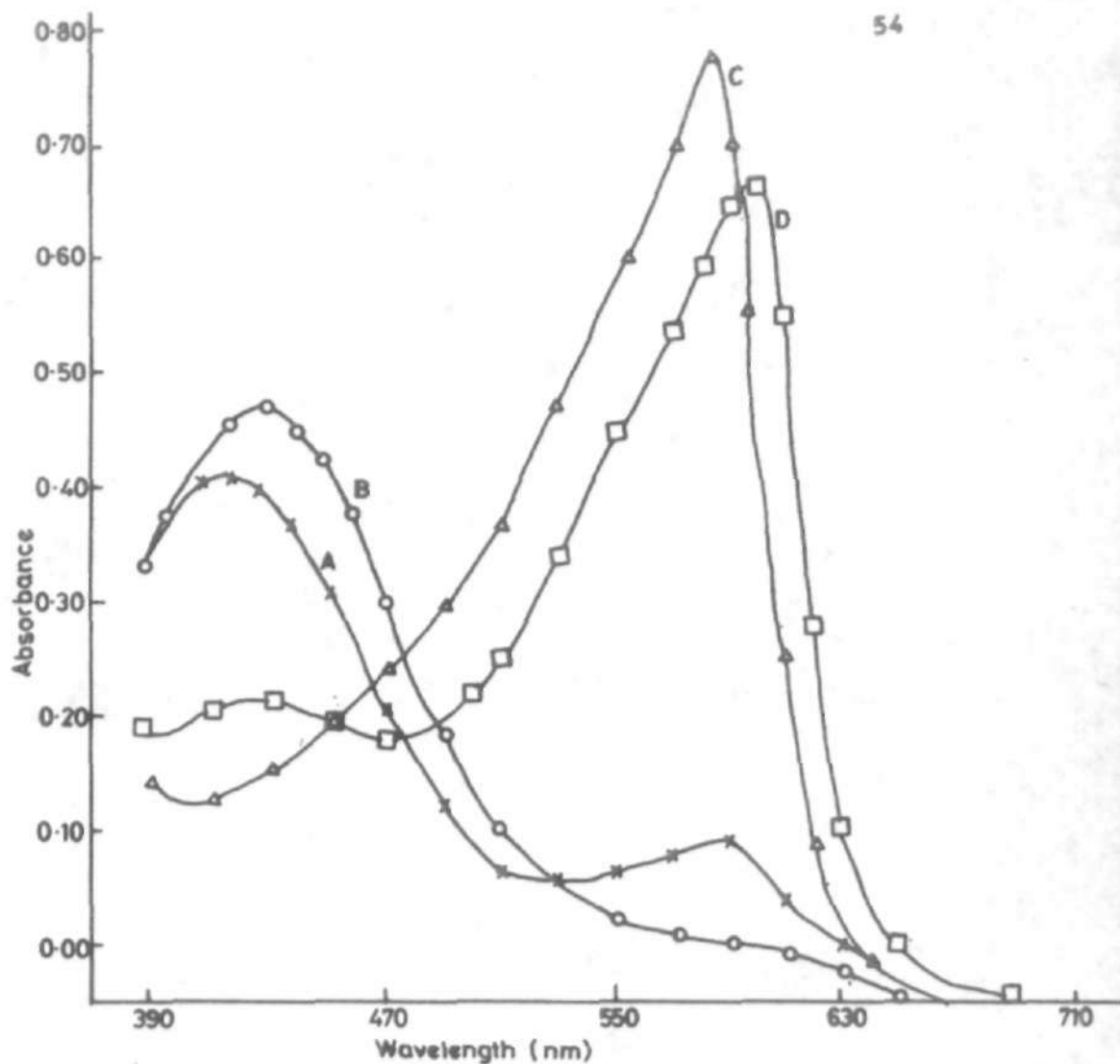


Fig. 2.10 Absorption spectra: showing the effect of pH on XO and XO-CTAB systems.

[XO =  $2.4 \times 10^{-5} \text{M}$ ] [CTAB =  $4 \times 10^{-4} \text{M}$ ]

Curve A: XO pH 4.5; Curve B: XO+CTAB pH 4.5

Curve C: XO pH 10.5; Curve D: XO+CTAB pH 10.5

This phenomenon that results in a shift in wavelength of absorption maximum has been explained by the preferential absorption of one dissociated form of the indicator onto the surfactant micelles with the consequent displacement of the acid-base equilibrium in favour of this form<sup>33</sup>.

Comparing the absorbance maxima of the acidic xylenol orange curves A and B, it is noted that the addition of CTAB results in a decrease by approximately a third of the maximum absorbance value. This suggests that a third of the ionizable forms of the xylenol orange as an acid is preferentially absorbed into the micellar systems.

From the experiments carried out, it is not evident which of the groups of the indicator are involved in the bond with the surfactant.

However this one third decrease in maximum absorbance of xylenol orange as a free acid, on addition of the surfactant is in agreement with the earlier proposition that the bond must involve the phenolic group whose ionizable hydrogen constitute a third of the ionizable forms of the indicator.

The two proposed systems of XO-CTAB would then be  $XO(CTAB)_2$  that is covalently bonded and  $XO(CTAB)_6$  which is composed of micellar aggregates in ion association.<sup>32</sup>

#### 2.4. Study on the interaction between XO/CTAB/M<sup>n+</sup>

where M<sup>n+</sup> is a metal ion e.g. of Cd, Cr, Ni, Cu, Mn, Fe, Zn, Co, and Ca.

##### Reagents:

(i) M<sup>n+</sup> 3.2 x 10<sup>-5</sup> M

4 x 10<sup>-2</sup> M solutions of the following metal ions:- Fe (iii) Cd, Cr, Ni, Cu, Mn, Zn, Co and Mn were prepared in different 1 litre standard volumetric flasks by dissolving the appropriate weights of the metallic salt (nitrate where available) in distilled deionized water and making the solution to 1 litre with the same water. These stock solutions were appropriately diluted with distilled deionized water to give the required 3.2 x 10<sup>-5</sup> M solutions.

##### 2.4.1 Interaction of XO/CTAB complex, with metal ions: M<sup>n+</sup>

This was studied by observing the U.V. spectra of the complexes of the metal ions with XO/CTAB complex.

### Method

2cm<sup>3</sup> of the alkaline xylenol orange solution was accurately measured into a 50cm<sup>3</sup> standard flask. 10cm<sup>3</sup> buffer solution of pH 10.5 was added followed by 20cm<sup>3</sup> of the 4x10<sup>-4</sup>M CTAB solution and 5cm<sup>3</sup> of Mn<sup>+</sup> solution. The solution mixture in the flask was made up to the 50cm<sup>3</sup> mark with distilled deionized water. Using the SP1750 B spectrophotometer and reagent blank containing the same concentrations of XO and CTAB and buffer as in the experimental solution, the absorbance of the solution at various wavelengths was measured one hour after mixing the components.

This experiment was done for all the metal ions.

### Results:

Fig 2.10 a, b, and c show the spectra of the various metal ions in the presence of XO and CTAB.

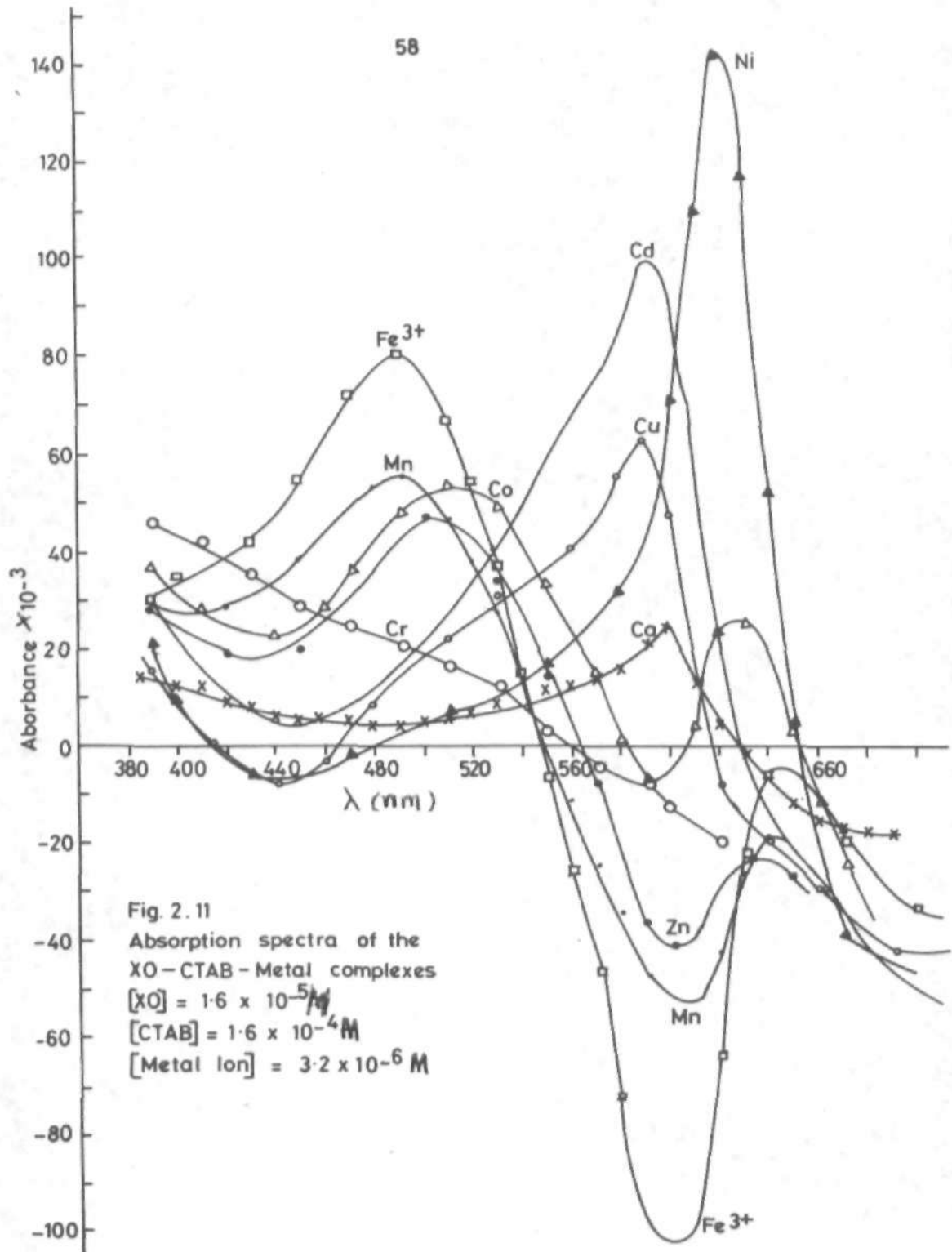
### Result

The metal complexes of XO-CTAB investigated absorbs between 490nm and 630nm.

The complexes of Fe, Mn, Zn and Co have  $\lambda_{max}$  at about 490nm.

This means that these ions will interfere seriously in the





determination of one another using the XO-CTAB complex.

The complexes of Cd, Cu and Ca have a maximum at about 600nm, and will therefore interfere in the determination of one another.

The complex of Ni, Co, and  $Fe^{3+}$  absorb at about 680nm and each metal ion will show a serious interference in the determination of each other.

From these results the system Ni-XO-CTAB was selected for further study in this work because of the following reasons and observations:-

(i) The absorbance of the  $Mn^{2+}$ -XO-CTAB complex is highest for the nickel complex. This implies that nickel complex has the highest molar absorptivity and hence the greatest sensitivity among the metal complexes studied.

(ii) The pattern of the different spectra shows that the wavelength of maximum absorbance ( $\lambda_{max}$ ) of the nickel complex stands farthest away from those of the other metal complexes. This implies that the interference due to other metal ions would be least for the nickel complex hence the highest selectivity will be shown by the nickel complex reaction.

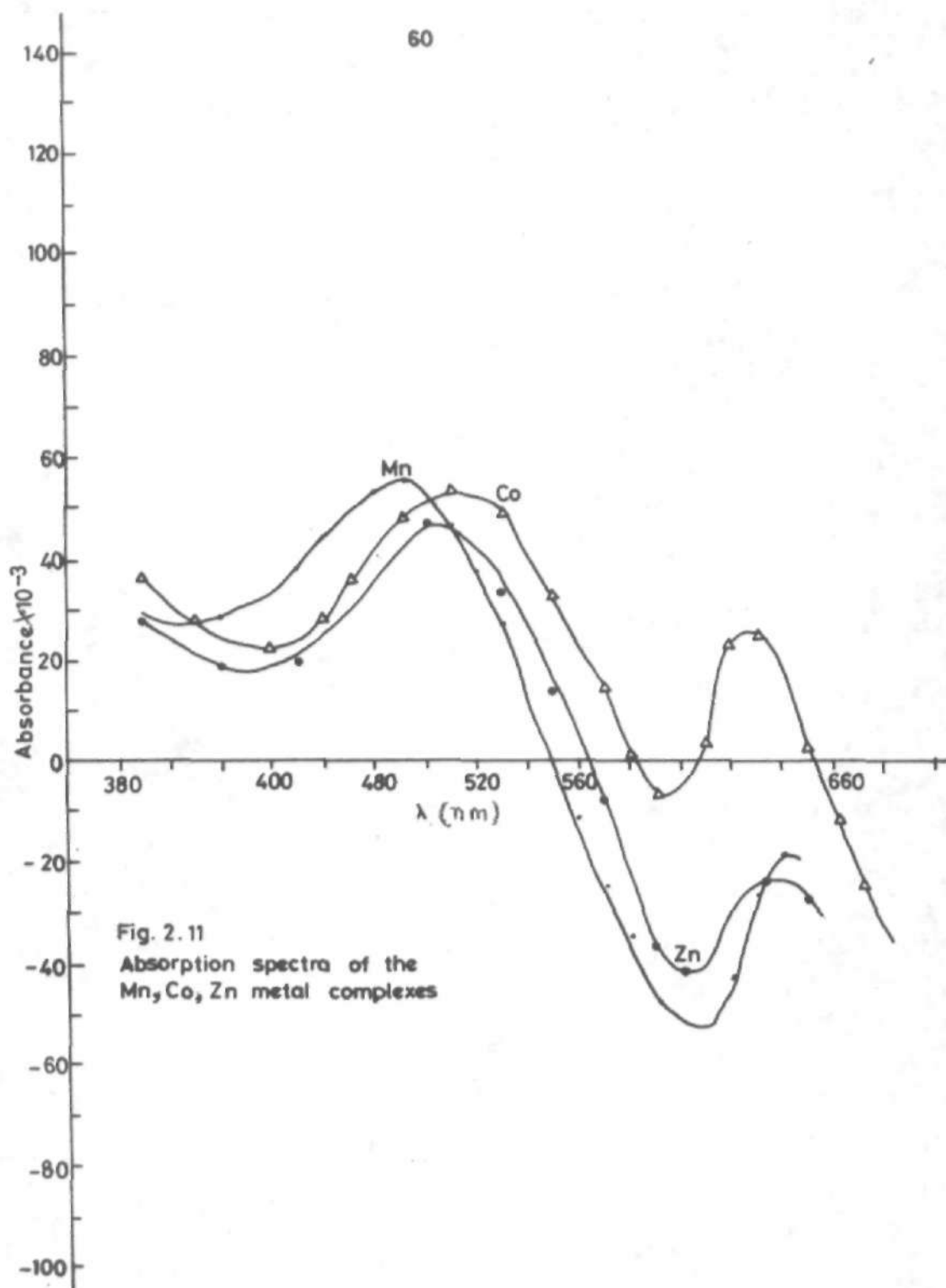


Fig. 2.11  
Absorption spectra of the  
Mn, Co, Zn metal complexes

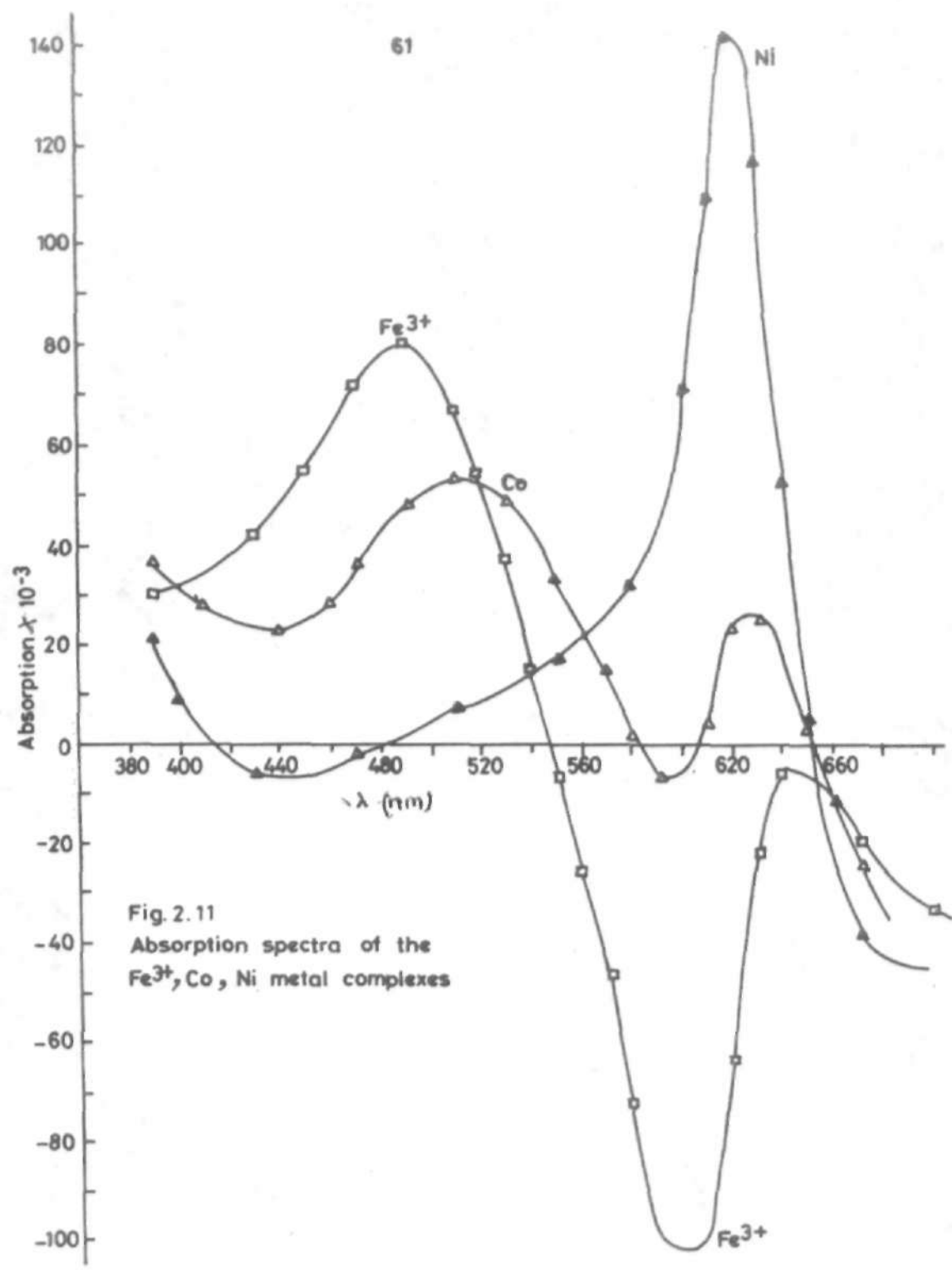


Fig. 2.11  
Absorption spectra of the  
Fe<sup>3+</sup>, Co, Ni metal complexes

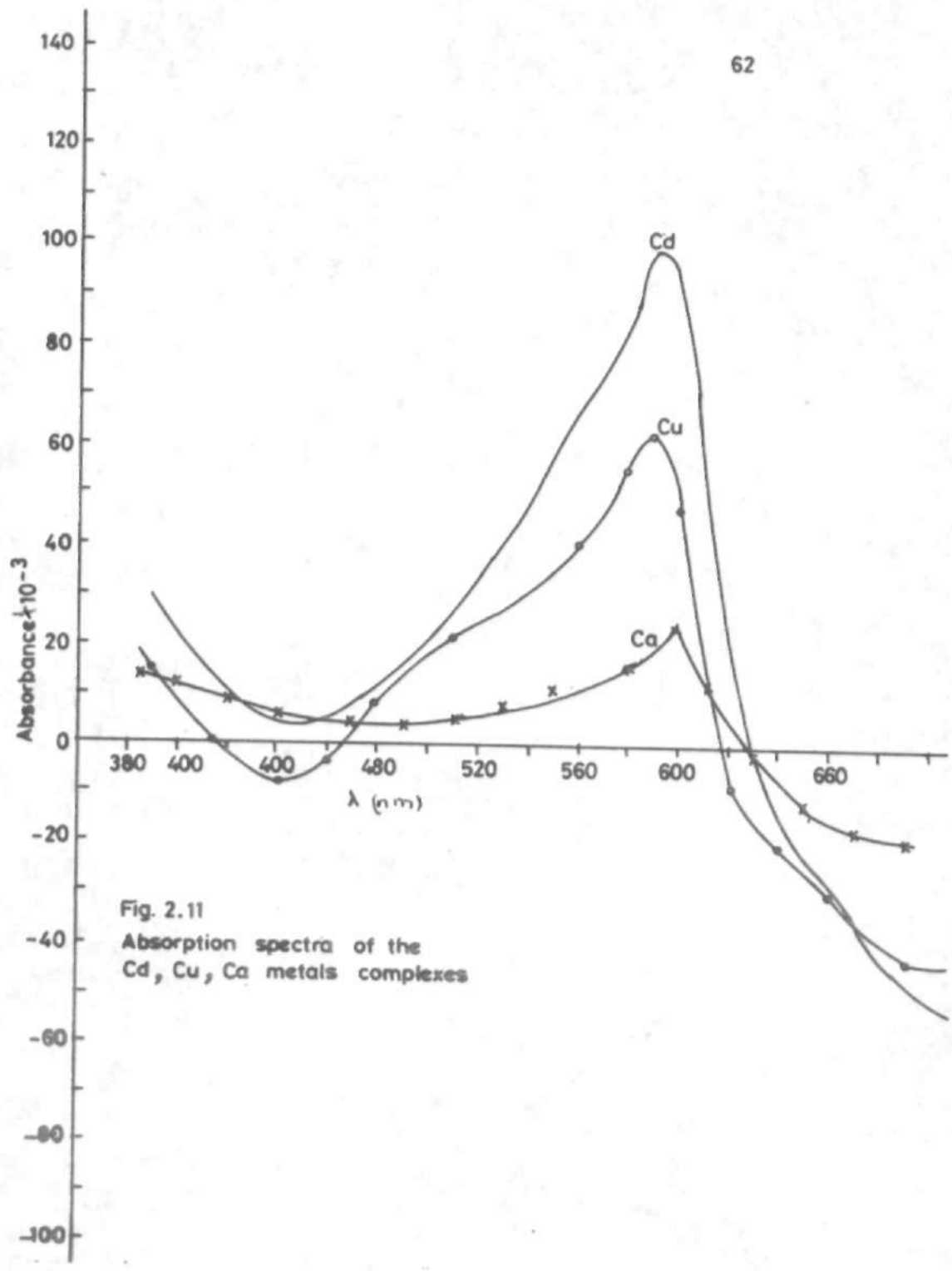


Fig. 2.11  
Absorption spectra of the  
Cd, Cu, Ca metals complexes

## CHAPTER THREE

Spectrophotometric Determination of Nickel Using  
Cetytrimethylammonium Bromide (CTAB) as a  
Surfactant and Xylenol Orange (XO) as Indicator.

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Spectrophotometric determination of nickel using  
Cetyltrimethyl Bromide CTAB as a surfactant and  
Xylenol orange XO as indicator.

3.1. Introduction:

The number of spectrophotometric methods for the determination of nickel at trace level are relatively few. The most widely used colorimetric reagent for nickel is dimethylglyoxime. When dimethylglyoxime is added to an alkaline solution of a nickel salt which has been treated with an oxidising agent eg. bromide, red coloured complex of nickel at a higher oxidation state of 3 or 4 is obtained.<sup>35</sup> This complex absorbs at about 445nm and has a molar absorptivity<sup>36</sup> of  $1.36 \times 10^4$ .

Unless very large samples are taken however, this method does not readily afford means of assessing nickel at 1ppm level which is frequently encountered in the analysis of certain materials like steel and alloy.

A highly sensitive spectrophotometric method for the determination of nickel has been recorded by W.J. de Wet<sup>20</sup> and G.E. Behrens.<sup>20</sup>

This method was based on complex formation with the metallochromic indicator xylenol orange XO and the long chain quaternary

ammonium salt, cetylpyridinium bromide CPB. The blue complex formed has a formula  $\text{Ni}[\text{XO}(\text{CPB})_2]_2$  and a molar absorptivity of  $2.78 \times 10^4$  at 618nm.

This method affords the determination of nickel from 0.1ppm to 0.5ppm.

### 3.2. The New Method

The new method of spectrophotometric determination of nickel is based on a complex formation between nickel, xylenol orange XO and cetyltrimethylammonium bromide CTAB. The processes in the development of the method include a study of the following:

- (i) Spectral characteristics of Ni-XO and Ni-XO-CTAB systems.
- (ii) Effect of time on the colour development of the various complexes.
- (iii) Effect of reagent concentration on the complex Ni-XO-CTAB.
- (v) Range for Beer's law or limits of detection of nickel
- (vi) Precision of the method,
- (vii) Interfering elements/selectivity of the method
- (viii) Characterisation of the complex.

### 3.2.1 Reagents and Solutions

#### (i) Nickel $3.2 \times 10^{-5} \text{M}$ stock solution

Nickel chloride of the analytical grade was used without further purification.

9.52gm of the  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  was dissolved in  $1000\text{cm}^3$  standard volumetric flask with distilled deionized water. The solution was made up to the mark with the same water. This gave  $4 \times 10^{-2} \text{M}$  solution. A further 25 times dilution of this gave  $3.2 \times 10^{-5} \text{M}$  solution. Each dilution was carried out with distilled deionized water.

#### (ii) Alkaline xylenol orange stock solution $4 \times 10^{-4} \text{M}$ , pH 10.5

Xylenol orange was of the reagent grade and there was no further purification.

Preparation of the alkaline solution was as in 2.2.1

#### (iii) CTAB ( $4 \times 10^{-3} \text{M}$ ) and ( $4 \times 10^{-4} \text{M}$ ) stock solutions:

1.458g of CTAB were dissolved in a litre standard volumetric flask with distilled deionized water. The solution was made the  $1000\text{cm}^3$  mark with distilled deionized water.

This gave the  $4 \times 10^{-3} \text{M}$  stock solution. A ten times dilution of this gave the  $4 \times 10^{-4} \text{M}$  stock solution.

(iv) NaHCO<sub>3</sub>/NaOH buffer pH 9.7 to 10.7

The solid NaHCO<sub>3</sub> and NaOH samples were of the analytical grade and were used without further purification. A  $5 \times 10^{-2} \text{M}$  solution of NaHCO<sub>3</sub> was prepared by dissolving 4.2g of the salt in 1 litre standard flask. Also 0.1.M. NaOH solution was prepared by dissolving 4g of the hydroxide pellets and making it up to the mark in one litre standard flask with distilled deionized water.

To obtain buffer solutions of different pH values, 50cm<sup>3</sup> of the NaHCO<sub>3</sub> solution was mixed with x cm<sup>3</sup> of the NaOH solution and diluted to 100cm<sup>3</sup> in a standard 100cm<sup>3</sup> flask with distilled deionized water, where x has the following values for the various buffer values of pH.

x(cm <sup>3</sup> )	6.2.	9.1	10.7	15.2	17.8	19.1	20.2
pH	9.7	9.9	10	10.3	10.5	10.6	10.7

(V)  $M^{n+}$   $3.2 \times 10^{-5}M$  stock solution

where  $M^{n+}$  = ions of Cr, Co, Zn, Cu, Mn, Cd, Ca Fe N.

Appropriate weight of a salt of each of the metals was dissolved in a litre flask with distilled deionized water, to give a  $4 \times 10^{-2}M$  solution on making up the solution to the  $1000\text{cm}^3$  mark with same water. Dilutions to  $3.2 \times 10^{-5}M$  solutions were made for each metal as described in 3.2.1 (i).

3.2.2 Spectra Study

Method: for Ni-XO system

$3\text{cm}^3$  of the alkaline  $4 \times 10^{-4}M$  XO solution was accurately measured into a  $50\text{cm}^3$  standard flask.

$10\text{cm}^3$  of the buffer solution at pH 10.5 was added followed by  $5\text{cm}^3$  of  $3.2 \times 10^{-5}M$  nickel solution. The solution in the flask was made up to the mark with distilled deionized water. Using the Sp1750B UV spectrophotometer, the absorbance of the solution at various wavelengths were measured using a blank solution not containing nickel but otherwise the same as the sample solution. Measurements were done thirty minutes after mixing of the reagents.

A graph of absorbance against wavelength was plotted, fig 3.1 curve A.

Method for Ni-XO-CTAB

3cm<sup>3</sup> of the alkaline 4x10<sup>-4</sup>M XO solution was accurately measured into a 50cm<sup>3</sup> standard flask.

20cm<sup>3</sup> of 4x10<sup>-4</sup>M CTAB was added followed by 10cm<sup>3</sup> of the buffer solution of pH 10.5. Then 5cm<sup>3</sup> of 3.2x10<sup>-5</sup>M nickel solution was added. The solution was made up to the mark with distilled deionized water.

The absorbance of the solution at various wavelengths were measured on the spectrophotometer. The blank used was of the same concentration in XO, CTAB and buffer as the sample but without nickel.

A graph of absorbance versus wavelength was plotted.

Fig 3.1, curve A shows the absorption spectra of 2.4x10<sup>-5</sup>M XO in the presence of 3.2x10<sup>-6</sup>M nickel. Curve B shows the effect of addition of 1.6x10<sup>-4</sup>M CTAB, on the system that gave curve A.

It was found that on the additional of nickel solution to the XO-CTAB system, a deep blue colour was formed.

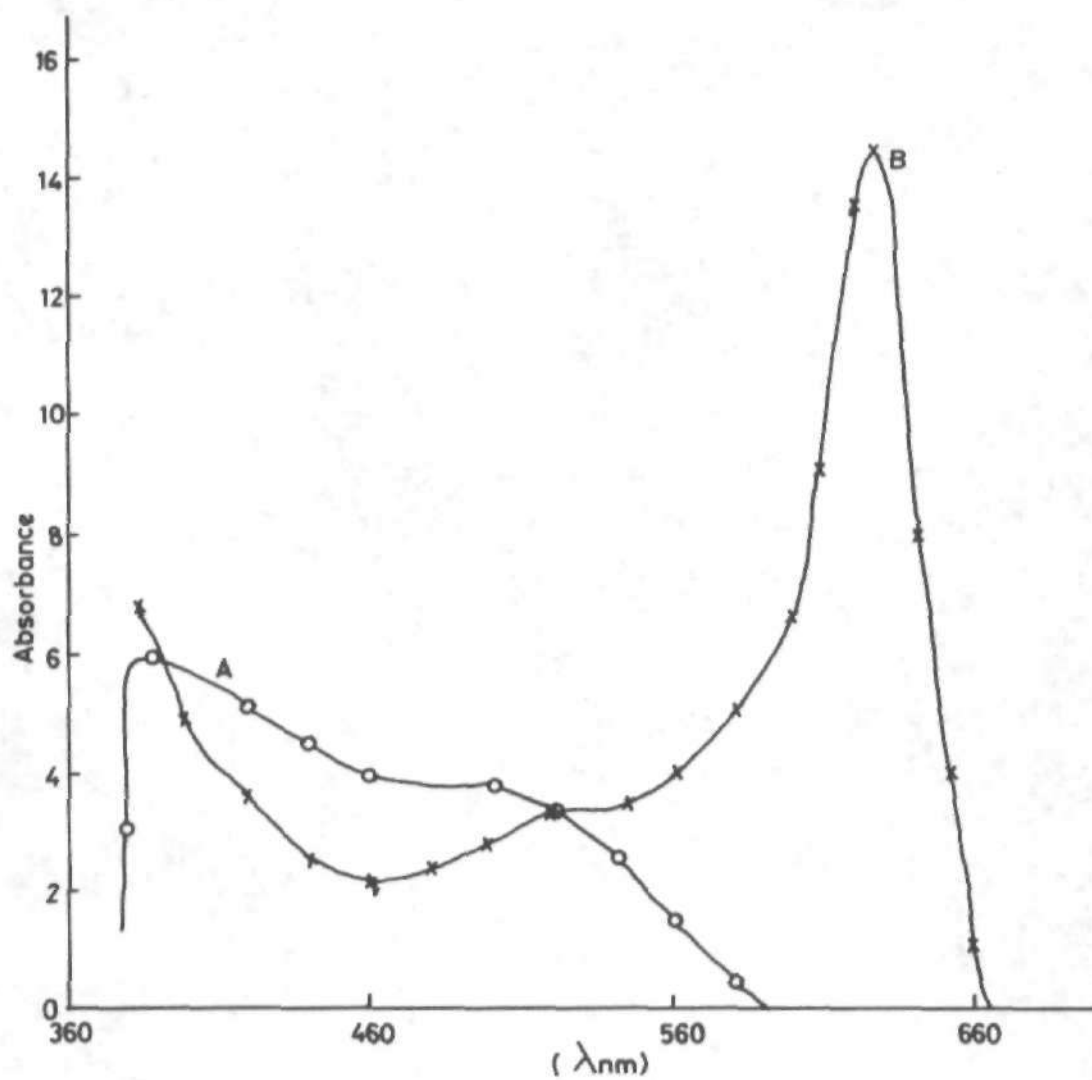


Fig. 3.1. The absorption spectra of some nickel complexes.  
 Curve I, Ni-XO and Curve II, Ni-XO-CTAB  
 using the reagent concentrations of  $[Ni]=3.2 \times 10^{-6}M$   
 $[XO]=2.4 \times 10^{-5}M$  and  $[CTAB]=1.6 \times 10^{-4}M$ .



There was a marked increase in the absorbance of nickel complex formed with XO when CTAB was added. There was also a considerable bathochromic shift, of about 122nm from 500nm to 622nm.

The marked increase in absorbance indicates a high increase in the sensitivity of the method for Ni determination by the presence of the surfactant CTAB.

Comparing fig 2.3a and fig 3.1, curve B it is noted that the absorbance of the reagent blank CTAB-XO is small at the wavelength of maximum absorbance 622nm of the Ni-XO-CTAB complex thus providing an ideal condition for analytical measurements.

### 3.2.3. Colour of the Solution of the Ni-XO-CTAB complex and time of standing prior to absorbance measurement.

The stability of the deep blue colour of the solution of Ni-XO-CTAB was studied at room temperature by measuring the absorbance of the complex at regular intervals.

#### Method:

1 cm<sup>3</sup> of 4x10<sup>-4</sup>M XO, 12cm<sup>3</sup> of 4x10<sup>-4</sup>M CTAB, 10cm<sup>3</sup> of the buffer solution pH 10.5 and 2cm<sup>3</sup> of 3.2x10<sup>-5</sup>M nickel solutions were mixed in a 50cm<sup>3</sup> standard flask.

The solution was made up to the 50cm<sup>3</sup> mark with distilled deionized water. After five minutes of mixing the reagents, the absorbance of the solution at 622nm was measured.

The blank used was of the same concentration in XO, CTAB and buffer as the sample but without nickel. The readings were taken at suitable intervals for one hour and after, at intervals of one day for seven days,

fig 3.2.

The results show that maximum and constant absorbance was obtained after about sixteen minutes. The absorbance remained constant for at least seven days.

#### 3.2.4. Effect of pH on the absorbance of Ni-XO-CTAB complex

Sodium bicarbonate/sodium hydroxide buffer solutions of various pH values were used. The absorbance was measured against reagent blank containing the same concentration of XO, CTAB and buffer as the sample solution but without nickel.

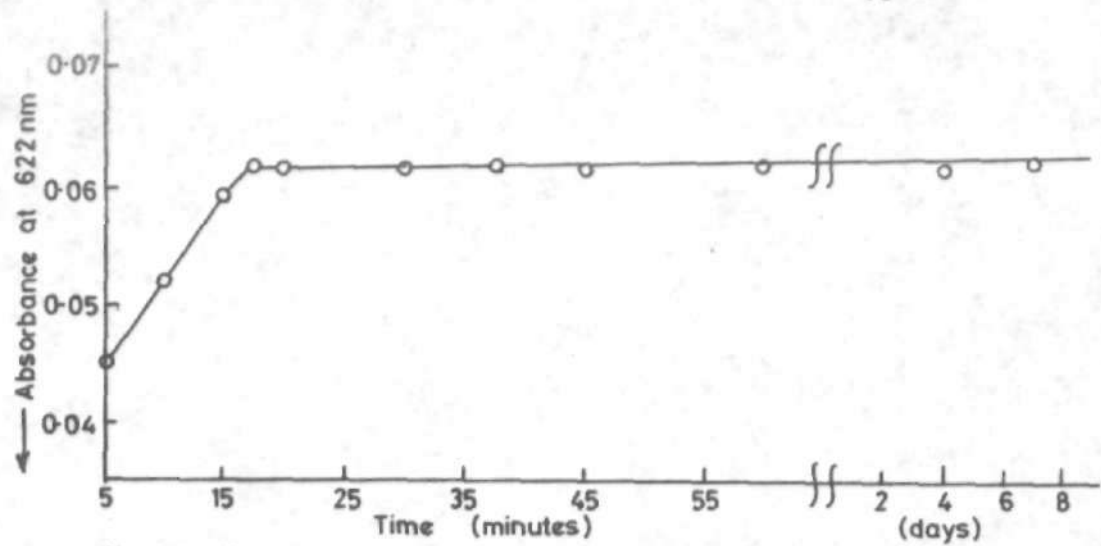


Fig. 3.2 Variation of absorbance of Ni-XO-CTAB in solution with time of waiting.

$$[XO] = 8 \times 10^{-6} M; [CTAB] = 9.6 \times 10^{-5} M; [Ni] = 1.28 \times 10^{-6} M.$$

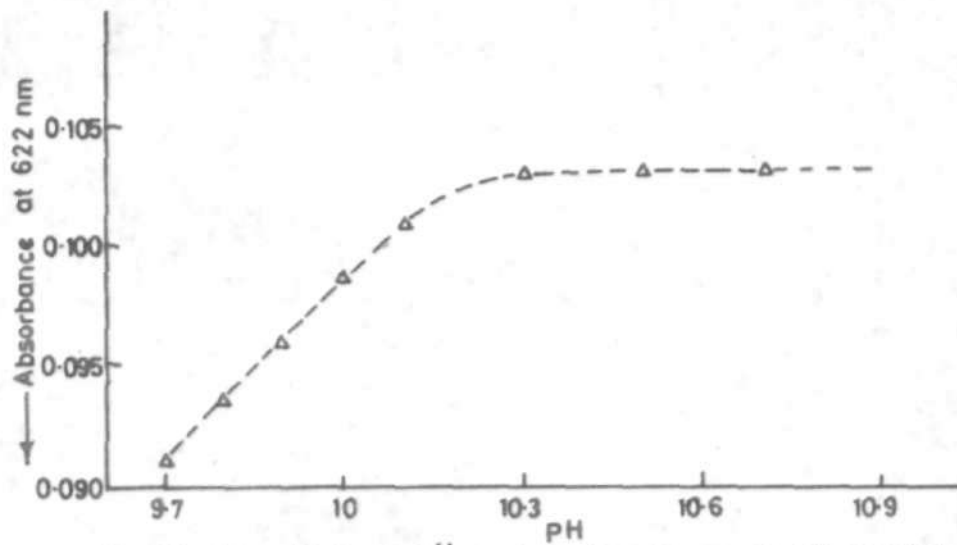


Fig. 3.3. The effect of pH on the absorbance of Ni-XO-CTAB complex.

$$[XO] = 1.6 \times 10^{-5} M; [CTAB] = 1.6 \times 10^{-4} M; [Ni] = 2 \times 10^{-5} M$$

Method:

2cm<sup>3</sup> of the alkaline 4x10<sup>-4</sup>M xylenol orange solution was accurately measured into a 50cm<sup>3</sup> standard flask. 20cm<sup>3</sup> of 4x10<sup>-4</sup>M CTAB solution was added followed by 10cm<sup>3</sup> of a buffer solution. 2cm<sup>3</sup> of the 3.2x10<sup>-5</sup>M nickel solution was added and the solution made up to the 50cm<sup>3</sup> mark with distilled deionized water. After 20 minutes of mixing the solutions, the absorbance of the solution at 622nm was measured using the spectrophotometer.

This experiment was repeated using the different pH buffer solutions but with the same concentration of XO, CTAB and nickel. In each case the pH of the sample solution was measured using the pH meter.

A graph of the absorbance of each solution against the pH of the solution was plotted, fig.3.3.

The result of the experiment showed that the absorbance values of the complex was pH dependent and reached maximum at pH of about 10.3.

A pH of 10.5 was chosen for further work.

3.2.5. Effect of reagent concentration on formation of the complex Ni-XO-CTAB.

This was studied by observing the change in absorbance of the solution with change in the concentration of (i) XO and (ii) CTAB.

Method:

3.2.5 (i) Change in XO Concentration

From  $1\text{cm}^3$  to  $6\text{cm}^3$  of  $4 \times 10^{-4}\text{M}$  XO solution were measured into a series of  $50\text{cm}^3$  standard flask.  $20\text{cm}^3$  of  $4 \times 10^{-4}\text{M}$  CTAB solutions was accurately measured into each flask, followed by  $10\text{cm}^3$  of the buffer solution. Lastly  $5\text{cm}^3$  of  $3.2 \times 10^{-5}\text{M}$  nickel solution was added into each flask. Each solution was made up to the  $50\text{cm}^3$  mark with distilled deionized water. After twenty minutes, the absorbance of each solution was measured at  $622\text{nm}$  using the SP1750 B spectrophotometer.

The graph of absorbance against the concentration of XO was plotted, fig 3.4 curve A.

The blank used was the same as the sample solution but without nickel. The results show a linear increase in absorbance with XO concentration to about six fold molar excess of XO relative to nickel when the absorbance starts decreasing with XO concentration. To be within the linear portion of the graph, a not more than six fold molar excess of XO relative to nickel was used for further work.

### 3.2.5.2. Change in CTAB Concentration

#### Method:

3 cm<sup>3</sup> of 4 x 10<sup>-4</sup> M XO was measured into each of a series of 50 cm<sup>3</sup> standard flask. From 1 cm<sup>3</sup> to 10 cm<sup>3</sup> of 4 x 10<sup>-3</sup> M CTAB were transferred into the series of flasks. 10 cm<sup>3</sup> of the buffer solution of pH 10.5 was added followed by 5 cm<sup>3</sup> of the 3.2 x 10<sup>-5</sup> M nickel solution. The absorbance of each solution at 622 nm was measured on the SP 1750 B spectrophotometer. The blank contained the same concentration of XO, CTAB and buffer as the sample solution but without nickel.

The graph of absorbance against concentration of CTAB was plotted fig 3.4 curve B.

The results in fig 3.4 show that the absorbance of the complex increases with increase in CTAB concentration up to a 3: 40 ratio of XO: CTAB and then starts decreasing as from 3:50 ratio of XO: CTAB.

For further work a ratio of XO: CTAB greater than 3:50 was used.

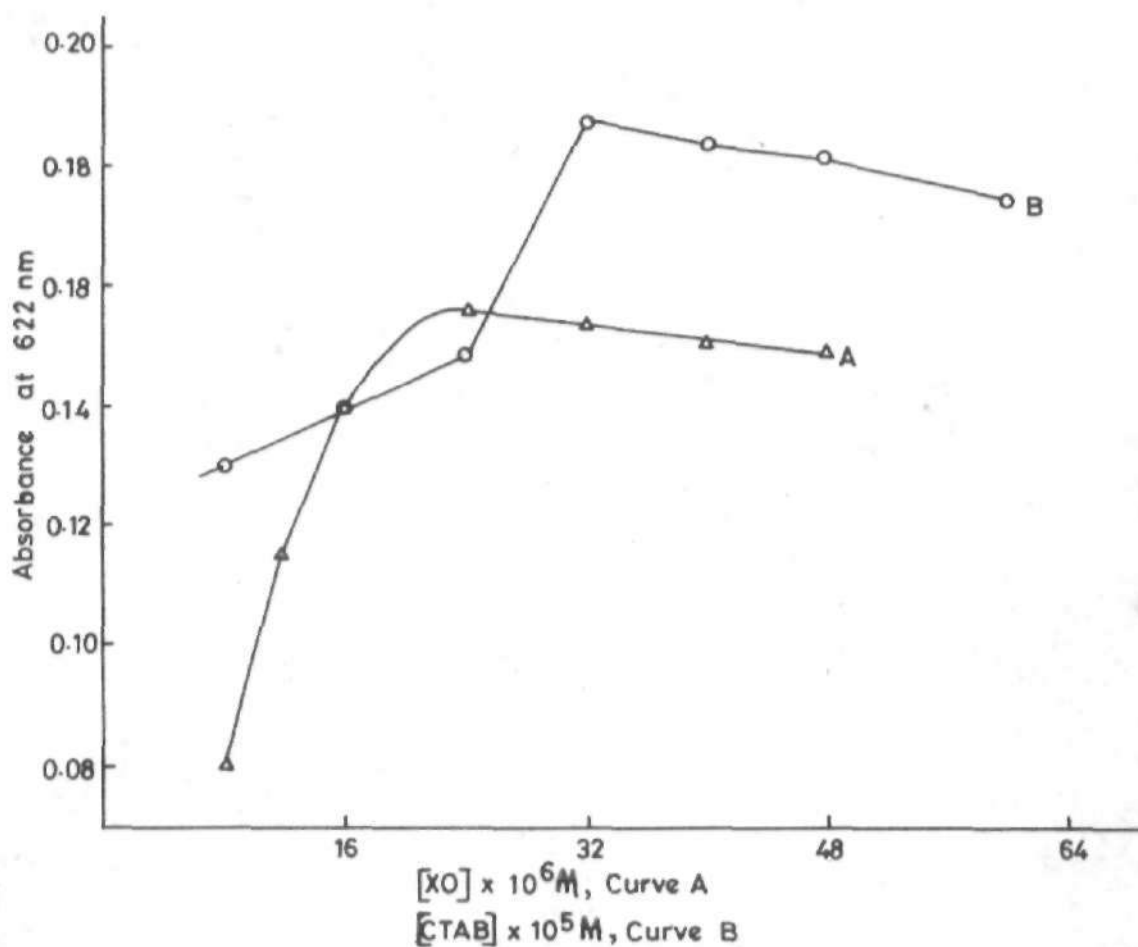


Fig. 3-4 Effect of concentration of reagents on Ni-XO-CTAB complex.  
 Curve A: Variation of absorbance with XO concentrations  
 $[Ni] = 3.2 \times 10^{-6} M$ ;  $[CTAB] = 1.6 \times 10^{-4} M$   
 Curve B: Variation of absorbance with CTAB concentrations  
 $[Ni] = 3.2 \times 10^{-6} M$ ;  $[XO] = 2.4 \times 10^{-5} M$

### 3.2.6. Beers Law and sensitivity of the method

#### 3.2.6.1 Preparation of the Calibration Curve

This was done by transferring  $3\text{cm}^3$  of  $4 \times 10^{-4}\text{M}$  XO solution,  $4.5\text{cm}^3$  of  $4 \times 10^{-3}\text{M}$  CTAB solution,  $10\text{cm}^3$  of the buffer solution of pH 10.5, and from  $0.5\text{cm}^3$  to  $12\text{cm}^3$  of  $3.2 \times 10^{-5}\text{M}$  nickel solution into a set of  $50\text{cm}^3$  standard flasks. Each solution was made up to the  $50\text{cm}^3$  mark with distilled deionized water. After 20 minutes the absorbance at  $622\text{nm}$  of each solution was measured on the spectrophotometer. The blank contained the same concentrations of XO, CTAB, and buffer solution as the sample solution but with no nickel.

This experiment was repeated using different volumes of the XO and CTAB solutions. Fig 3.5 shows the graphs of absorbance against concentration of nickel for different XO/CTAB concentrations but same XO:CTAB ratio of 1:15.

The calibration graph, fig 3.5 A, shows that Beer's law is obeyed up to 0.34 ppm nickel.

The optimum range for absorbance for the various calibration curves fig 3.5 A to fig 3.5 D is shown in table 3.1.



Calibration Curve:	XO	CTAB	Slope	Ni limit up to
A	$2.4 \times 10^{-5} \text{M}$	$3.6 \times 10^{-4} \text{M}$	0.039	0.34ppm
B	$3.2 \times 10^{-5} \text{M}$	$4.8 \times 10^{-4} \text{M}$	0.032	0.36ppm
C	$1.6 \times 10^{-5} \text{M}$	$2.4 \times 10^{-4} \text{M}$	0.032	0.23ppm
D	$0.8 \times 10^{-5} \text{M}$	$1.2 \times 10^{-4} \text{M}$	0.023	0.15ppm
	$4.8 \times 10^{-5} \text{M}$	$7.2 \times 10^{-4} \text{M}$	0.031	0.45ppm

Table 3.1. Detection limit of nickel for different XO-CTAB concentrations.

From table 3.1. XO:CTAB is constant at 1:15 but the absorbance per  $6.4 \times 10^{-7} \text{M}$  of nickel represented by the slope changes with change in the concentration of XO.

A graph of slope against XO concentration was plotted fig 3.6.

From this graph, curve A of fig. 3.5. gave the highest absorbance for the same concentration of nickel. The concentrations  $2.4 \times 10^{-5} \text{M}$  XO and  $3.6 \times 10^{-4} \text{M}$  CTAB that gave curve A of fig 3.5 are recommended for this study. From this calibration curve the molar extinction coefficient was calculated to be  $6.14 \times 10^{-4} \text{M}$  for Ni in the complex Ni-XO-CTAB at 622nm.

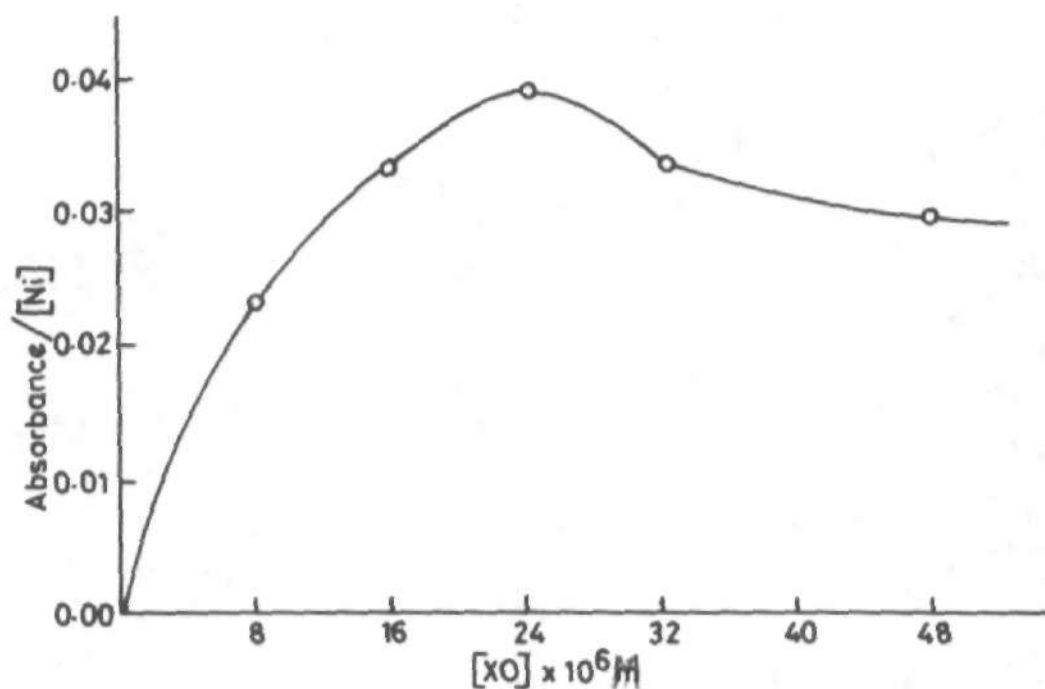


Fig. 3-6 Variation of absorbance of  $6.4 \times 10^{-7} \text{M}$  nickel in Ni-XO-CTAB complex with XO concentration; keeping XO:CTAB ratio constant at 1:15.

The value of molar extinction coefficient for Ni from some of the earlier methods are reproduced for comparison.

Reagent	Molar Extinction Coefficient
Dimethylglyoxime <sup>32</sup>	$1.36 \times 10^4$
XO/CPB <sup>20</sup>	$2.78 \times 10^4$
Furoin Semicarbarzone <sup>37</sup>	$1.54 \times 10^4$

Table 3.2: Molar extinction coefficient for Ni from some earlier methods.

With a molar extinction coefficient of  $6.14 \times 10^4$  obtained, this propose method is regarded as being highly sensitive.

The molar extinction coefficient of some trace metals in their determinations involving an indicator and a surfactant are also reproduced for comparison.

Indicator	Surfactant	Metal	Molar extinction coefficient
Bromopyrogallol-Red (BPR) <sup>21</sup>	Hexadecyltrimethyl ammonium bromide	Fe	$5.2 \times 10^4$
Catechol Violet <sup>23</sup>	Cetyltrimethyl-ammonium bromide	Mb	$4.6 \times 10^4$
Catechol Violet <sup>23</sup>	Cetyltrimethyl-ammonium bromide	Sb	$3.0 \times 10^4$
BPR <sup>38</sup>	1,10 phenanthroline	Ag	$5.1 \times 10^4$

Table 3.3:

Molar extinction coefficient for some trace metals.

### 3.2.7. Precision of the method

To determine the precision of the new method in pure nickel solution, the same amount of nickel  $2.56 \times 10^{-6} \text{M}$  solution was determined ten times using the calibration curve A of fig 3.5.

The average absorbance was  $0.155 \pm 0.001$  and the error was 0.65% Table 3.4 shows these results.

---

Experimental No	1	2	3	4	5	6	7	8	9	10
Absorbance at 622nm	0.154	0.155	0.154	0.155	0.156	0.151	0.158	0.155	0.156	0.156
Mean with S.D.	= $0.155 \pm 0.001$									

---

Table 3.4: Absorbance for  $2.56 \times 10^{-6} \text{M}$  Nickel in 10 different Measurements

### 3.2.8. Interference Study:

The selectivity of the proposed method was investigated by the determination of  $2.56 \times 10^{-6} \text{M}$  nickel in the presence of a series of metals that are usually found in food stuff at trace level.

Method:

The absorbance of  $2.56 \times 10^{-6} \text{M}$  nickel was determined at 622nm using the method described in sections 3.2.1 to 3.2.7.

The absorbance of the same concentration of nickel in the presence of other ions in varying molecular concentrations relative to nickel was determined.

The change in absorbance was taken as a measure of interference and expressed in percentage. The result is shown in table 3.5.

Ion added:	Molar excess relative to Ni	Absorbance at 622nm	Interference %
Ni	-	0.155	-
Fe <sup>3+</sup>	1	0.135	-12.9
Fe <sup>3+</sup>	2	0.055	-64.5
Ca	1	0.156	+0.6
Zn	1	0.150	-3.2
Cd	1	0.160	+3.2
Cd	2	0.200	+29.0
Co	1	0.190	+22.6
Mn	1	0.154	- 0.6
Cu	1	0.155	- 0.0
Cu	2	0.157	+ 1.3
Cr	1	0.152	-1.9
Cr	2	0.145	-6.5

Table 3.5. Interference (%) of some metal ions in the new method of determination of nickel.

The results show that cobalt and iron (iii) interfere seriously in the determination of nickel.

Zinc and cadmium cause some interference while copper and manganese and chromium cause very little or no interference. No attempts were made in the present study to mask the interfering ions.

### 3.2.9. Composition of the Complex

Reagents: (i) Nickel ( $2 \times 10^{-4} \text{M}$ ) Solution

The  $4 \times 10^{-2} \text{M}$  nickel solution prepared as described in section 3.2.1 was diluted with distilled deionized water to give  $2 \times 10^{-4} \text{M}$  nickel solution.

(ii) CTAB  $4 \times 10^{-4} \text{M}$  Solution

This was prepared as in 3.2.1.

(iii) XO  $4 \times 10^{-4} \text{M}$  Solution

This was also prepared as in 3.2.1

(iv)  $\text{NaHCO}_3/\text{NaOH}$  buffer at pH 10.5

This was prepared as in 3.2.1

The composition of the complex Ni-XO-CTAB was investigated by mole ratio method.

Method A (i) With a constant nickel concentration and varying concentration of XO and CTAB but keeping XO:CTAB ratio constant.

From  $1\text{cm}^3$  to  $8\text{cm}^3$  of  $4 \times 10^{-4}\text{M}$  XO solution were accurately measured into a set of  $50\text{cm}^3$  standard flasks.

A calculated volume of CTAB solution was added into each flask so that the ratio of XO:CTAB remained constant at 1:6:  $10\text{cm}^3$  of the buffer solution was added into each flask followed by  $1\text{cm}^3$  of  $2 \times 10^{-4}\text{M}$  nickel solution. Each solution was then made up to the  $50\text{cm}^3$  mark with distilled deionized water.

After 20 minutes the absorbance of each solution was measured at  $622\text{nm}$  using reagent blank containing XO and CTAB of the same concentrations as in the sample but without nickel.

The unican SP1750 B spectrophotometer was used.

A graph of absorbance against concentration of XO was plotted fig. 3.7, curve A.

This experiment was repeated using the same Ni concentration

(ii) With constant Ni concentration, constant CTAB concentration and varying concentration of XO

From  $1\text{cm}^3$  to  $8\text{cm}^3$  of  $4 \times 10^{-4}\text{M}$  XO were measured into a set of  $50\text{cm}^3$  standard flask.  $25\text{cm}^3$  of  $4 \times 10^{-4}\text{M}$  CTAB was added into each flask followed by  $10\text{cm}^3$  of the buffer solution.  $1\text{cm}^3$  of the  $2 \times 10^{-4}\text{M}$  nickel solution was measured into each flask. Each solution was made up to the  $50\text{cm}^3$  mark with distilled deionized water. After 20 minutes, the absorbance of each solution was measured using the spectrophotometer. The measurements were done at  $622\text{nm}$  using reagent blank containing XO and CTAB of the same concentration as the sample but without nickel.

Fig 3.7, curve C shows the graph of the absorbance against the concentration of XO under the conditions described above. The results show that a stable complex is formed at a Ni:XO ratio of 1:4. This ratio is independent of the CTAB concentration and XO:CTAB ratios.



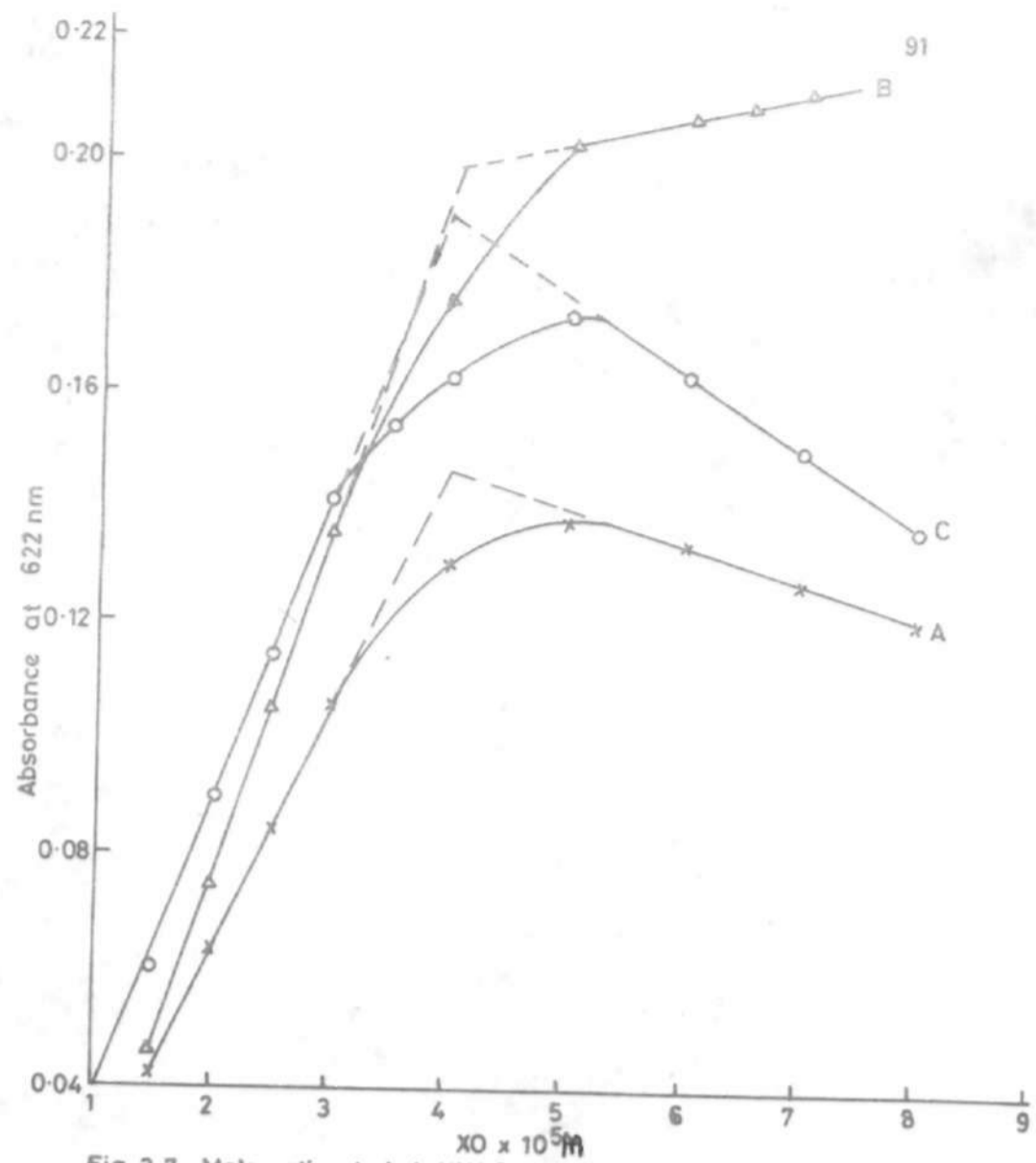


Fig. 3.7 Mole ratio study: Ni:XO in the complex Ni-XO-CTAB. Variation of absorbance of the complex with XO concentrations.

- A  $[Ni = 10^{-5} M]$  ; XO : CTAB 1 : 6
- B  $[Ni = 10^{-5} M]$  ; XO : CTAB 1 : 14
- C  $[Ni = 10^{-5} M]$  ; XO : CTAB =  $2 \times 10^{-4} M$  constant

Method B:

With constant concentration of XO and CTAB  
and varying concentration of Nickel

1cm<sup>3</sup> of 4x10<sup>-4</sup>M XO solution was accurately measured into each of a set of 50cm<sup>3</sup> standard flasks. 2cm<sup>3</sup> of 4x10<sup>-3</sup>M CTAB solution was added into each flask, followed by 10cm<sup>3</sup> of the buffer solution of pH 10.5.

Varying volumes of 3.2x10<sup>-5</sup>M nickel solution were measured into the flasks.

The solutions were made up to the 50cm<sup>3</sup> mark with distilled deionized water. After 20 minutes the absorbance of each solution was measured at 622nm using the reagent blank of the same concentrations in XO, CTAB and buffer as the sample but without nickel. The SP1750 B spectrophotometer was used.

The graph of absorbance against concentration of nickel was plotted, fig 3.8 curve A.

The entire experiment was repeated using different ratios of XO:CTAB concentrations.

Fig 3.8 curves A and B are of the same concentration of XO but different concentration of CTAB, while curves C and D have different concentrations of both XO and CTAB.

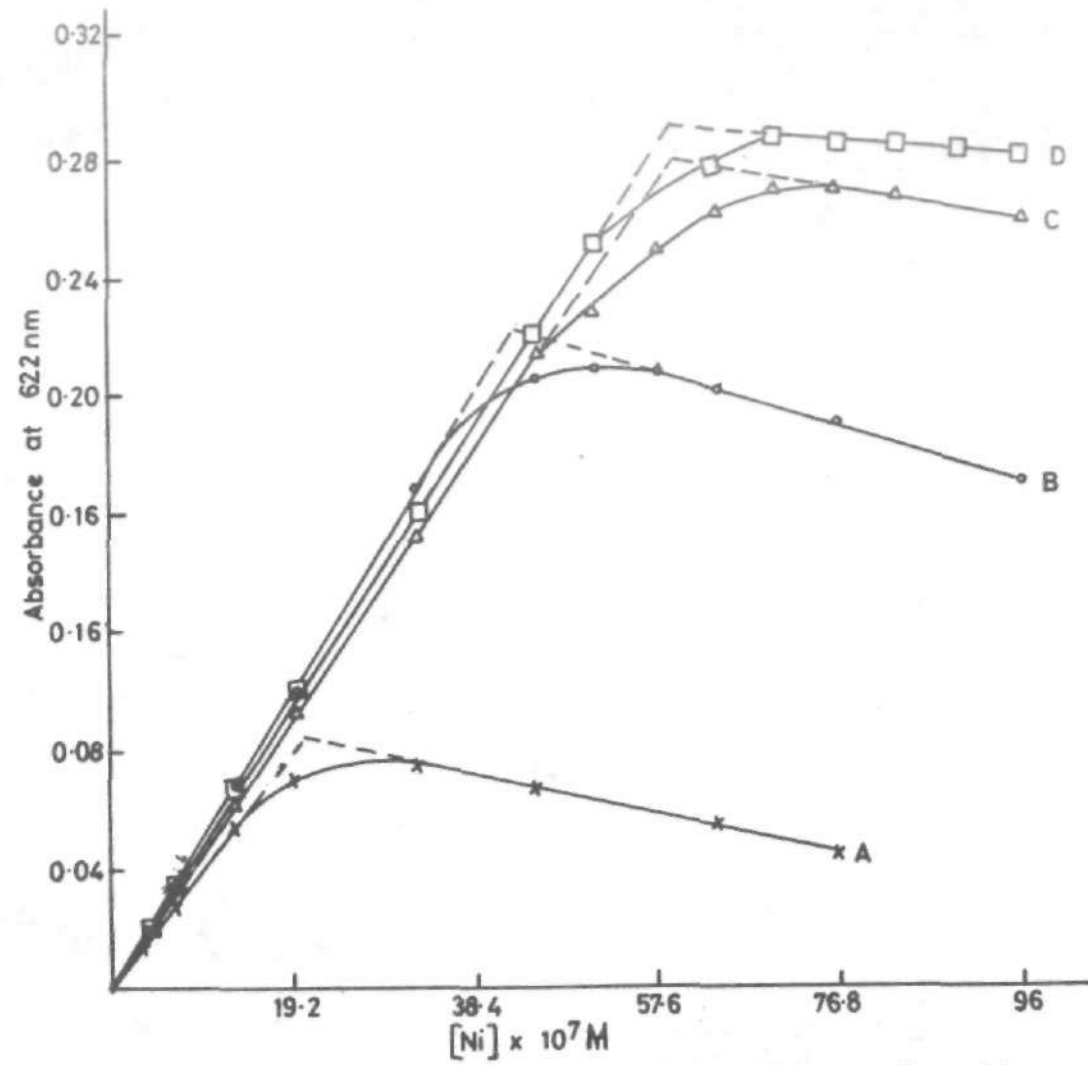


Fig. 3-8 Variation of absorbance of Ni-XO-CTAB complex with [Ni] in Ni:XO mole ratio study.

- A  $[XO = 8 \times 10^{-6} M]$ ;  $[CTAB = 1.6 \times 10^{-4} M]$   
 B  $[XO = 1.6 \times 10^{-5} M]$ ;  $[CTAB = 2.4 \times 10^{-4} M]$   
 C  $[XO = 2 \times 10^{-5} M]$ ;  $[CTAB = 3.2 \times 10^{-4} M]$   
 D  $[XO = 2 \times 10^{-5} M]$ ;  $[CTAB = 6.4 \times 10^{-4} M]$

The results as shown in the graphs of fig 3.8 indicate that the two segments of each graph when extrapolated meet at nickel:XO ratio of 1:4. This ratio is independent of CTAB concentration as shown by curves A and B and also independent of XO concentration as shown by A, C, D. Since it has been established in section 2.3.1. that XO and CTAB interact in the ratio of 1:2 and 1:6, where 1:6 may be as a result of micelle aggregation and 1:2 a covalent link with phenolic end of the Xylenol orange, then the formula of the complex would be  $\text{Ni}[\text{XO}(\text{CTAB})_2]_4$ . A formula of  $\text{Ni}[\text{XO}(\text{CTAB})_6]_4$  would represent the stoichiometry of the complex in micellar aggregates.

### 3.3. Conclusion

A highly sensitive spectrophotometric method for the determination of nickel in trace level has been established.

The method involves the formation of a blue complex between nickel, xylenol orange XO and cetyltrimethylammonium bromide as a surfactant.

The complex formed has a formula of  $\text{Ni} \left[ \text{XO CTAB}_6 \right]_4$  and absorbs at 622nm with a molar extinction coefficient of  $6.14 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$ .

Beer's Law is obeyed up to 0.34 ppm nickel.

To carry out the experiment for the determination of nickel, the calibration curve is prepared using  $2.4 \times 10^{-5} \text{M}$  XO,  $3.6 \times 10^{-4} \text{M}$  CTAB,  $10 \text{cm}^3$  of sodium bicarbonate/sodium hydroxide buffer of pH 10.5 and nickel concentration not exceeding  $4 \times 10^{-6} \text{M}$ , all in  $50 \text{cm}^3$  standard flask.

The measurement should be taken at least twenty minutes after mixing the reagents and with a reagent blank containing the same concentrations of XO, CTAB and buffer as the sample solution but without nickel.

The selectivity of the method is however limited due to serious interference by cobalt, cadmium and iron.

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