

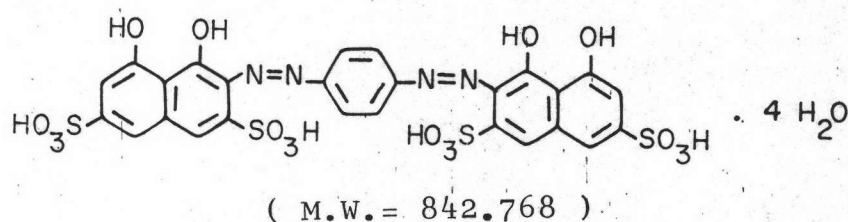
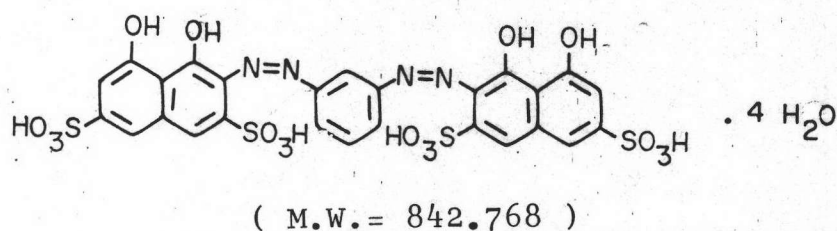


CHAPTER III

EXPERIMENTALS, RESULTS AND DISCUSSION

3.1 Preparation, Isolation and Purification of the Dyes.3.1.1 Preparation of the 1,3-bis(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)benzene: (m-X Dye) and 1,4-bis(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)benzene: (p-X Dye).

The proposed structures of the dyes are as follows respectively :

Reagents :

- (1) m- and p- phenylenediamine dihydrochloride,
 $C_6H_4(NH_2)_2 \cdot 2HCl$ (reagent grade, BDH) 98%
- (2) Chromotropic acid sodium salt, $C_{10}H_6O_8S_2Na_2$
(reagent grade, BDH)
- (3) Sodium nitrite (Analar, BDH)
- (4) Hydrochloric acid (Analar) density 1.18 g/ml
- (5) Sodium hydroxide (Analar, BDH)

Procedure:

Hydrochloric acid 20.5 ml (d=1.18 g/ml) was poured on ice (100 g) and the whole was cooled in a freezing mixture, to this was added a cold solution of sodium nitrite (3.75 g in 12.5 ml of water).

A previously prepared solution of m-phenylenediamine dihydrochloride for the synthesis m-X Dye (3.8 g of amine acidified with 2.5 ml hydrochloric acid) was immediately poured into the solution of nitrous acid. A yellow solution of the tetrazonium compound was produced instantaneously.

14.5 g of chromotropic acid (disodium salt) were dissolved in 5 g of sodium hydroxide in 50 ml of water. After cooling to -5°C in a freezing mixture, this solution was added, with constant stirring at about 5 ml a time, the solution of the tetrazonium salt. A deep red dye was obtained immediately. The solution was continuously stirred in the freezing mixture for about 30 minutes, and the appropriate amount of sodium hydroxide solution was then added to adjust the pH of the solution to 9 (observed by a pH meter).

The whole was evaporated to dryness on a steam bath. Subsequently the product was dried at 60°C for 24 hours in an oven. The crude m-X Dye was kept in a dark bottle for further isolation and purification.

For the preparation of p-X dye, the detailed experimental procedure was exactly the same as of m-X dye except p-phenylenediamine dihydrochloride was used in place of m-phenylenediamine dihydrochloride.

3.1.2 Isolation and Purification of m-X and p-X Dyes

Some impurities due to the excess of starting materials and the derivatives of dyes caused by the side reaction were expected to present in the crude dyes. It is consequently necessary that the following isolation and purification of dyes to be carried out.

About 2.0 g of crude dye was dissolved in 20 ml of 1 F NaOH and cooled in an ice bath, then gradually pour into 30 ml conc. hydrochloric acid with constant stirring (by using a magnetic stirrer) and stored in the refrigerator overnight. The precipitate was separated by centrifugation and finally rinsed with cold 6 F hydrochloric acid. The residue was dried at 60°C in an oven for 24 hours. The procedure was recycled and repeated for three times. The purity of the dye obtained was checked by applying a method of paper chromatography with suitable solvent systems. Detailed experiment and result are described in the following section.

3.1.3 Paper Chromatography of Dyes

In the paper chromatography of dye, generally partition chromatography is applied (23). The experiments

are a suitable chromatography paper, a solvent system and apparatus for developing the chromatogram. Sramek's study (24) on the selection of solvent systems for the partition paper chromatography of water soluble dyes gave the following conclusions. Firstly, the solvent system must always contain water and a further component enabling the formation of hydrogen bonds. Secondly, the solvent systems containing aliphatic, aromatic, hydrogenated, nitrated, chlorinated, or terpene hydrocarbons as a mobile phase are not suitable for the chromatography of dyes. Thirdly, suitable conditions for the chromatography are obtained with solvent systems containing alcohols, glycols, and ethers (substances containing functional OH groups) as a mobile phase. Especially suitable mobile phases are primary alcohols, in which cohesion of hydrogen bonds are characterized. Finally, in one-component aqueous solvent systems, the absorption effect is most important.

In this research work, various composition of mixed solvent systems were investigated by the ascending paper chromatography in order to determine the optimal condition for separating the pure dye from its impurity. The various composition of mixed solvent systems were shown in Table 3.1.



Table 3.1 The various composition of mixed solvent systems that used for determining m-X and p-X dyes.

| system no. | Solvent | Composition | Ref. |
|------------|---|---------------|-------|
| 1 | water | - | |
| 2 | methanol | - | |
| 3 | ethanol | - | |
| 4 | acetone | - | |
| 5 | ammonia solution 1% (v) | - | 25,26 |
| 6 | sodiumchloride 2.5% (w/v) | - | 25,26 |
| 7 | sodiumchloride 2% (w/v) in ethanol 50% | - | 25,26 |
| 8 | isobutanol : ethanol : water | 1:2:1, 5:3:2 | 25,26 |
| 9 | n-butanol:glacial acetic acid: water | 20:5:1 | 25,26 |
| 10 | isobutanol:ethanol:water = 3:2:2 and added 1 cc. of ammonia solution(sp.gr.0.91) in the mixed solvent 99 cc. | | 25,26 |
| 11 | phenol : water | 80:20 (w) | 25,26 |
| 12 | 2-butanone:acetone:water:ammonia solution | 350:150:150:1 | 25,26 |
| 13 | 2-butanone:acetone:water | 7:3:3 | 25,26 |
| 14 | ethylacetate:pyridine:water | 11:5:4 | 25,26 |
| 15 | trisodiumcitrate 2% (w/v) in ammonia solution 5% | - | 27 |
| 16 | water:hydrochloric acid(sp.gr 1.18) | 30:6.5 | 25,26 |

Table 3.1 cont.

| system no. | Solvent | Composition | Ref. |
|------------|---|-------------|------|
| 17 | pyridine:isopentanol:25% ammonia solution | 1.3:1:1 | 28 |
| 18 | n-butanol:pyridine:water | 0.5:1:1 | 28 |
| 19 | water:ammonia solution:n-butanol | 25:2:2 | |

Solvent systems of No.5-18 are the general standard systems recommended for the paper chromatographic identification of food and synthetic dyestuffs (25-28). The system of No.19 is developed in this work.

Ascending paper chromatographic experiments of m-X and p-X dyes using all nineteen developing solvent systems as described in the above table were carried out in order to find the optimal system which gave well separation and good chromatograms.

A few milligrams of the dyes were dissolved in a small amount of the mixed solvent system. A Whatman number 1 filter paper (15x23 cm) was spotted with a small amount of the dye of the distance of 2 cm. from the bottom and then dried in air. The paper was folded in a cylindrical shape and subsequently immersed into an enclosed container which was contained about 2 cm. height of each mixed solvent. The developing solvent was allowed to ascend to a premarked line on the paper (10 cm above the starting

point). Chromatogram was developed and completed in about a half an hour at room temperature. The paper was then removed from the chamber and was dried in air.

It was found that the solvent system of No.19 and No.8 appeared to be most suitable for m-X and p-X dye respectively.

After the third recrystallization of the dyes the paper chromatogram of m-X dye showed that the dye sample consisted of the major component had a purity more than 90% and an average R_f value is 0.50. For p-X dye, it showed one component with a purity of above 90% and had an average R_f value of 0.61.

3.2 Infrared Spectroscopy of Synthetic Dyes

Infrared spectrum can in theory be rigorously analyzed on the basis of fundamental principles. It can also be interpreted empirically using so-called "functional group frequencies" and the most characteristic physical property of a compound, serving as a "fingerprint".

Infrared spectroscopy can be enormously useful in the analysis of dyes (29).

(1) Pendant groups, of course, can be detected via the usual correlations, due consideration being given to intensities and the possibilities of overlapping.

(2) Groups involved in the chromophore can often be detected, although the usual correlations must be

applied with caution and frequency shifts must be expected.

(3) Pattern recognition remains a most valuable tool, since the dye may thereby be identified exactly; or a similar spectrum, which may establish at least a partial structure, may be found.

The spectral complexity of the dye usually results in a fairly crowded spectrum. Overlapping may conceal bands otherwise readily recognizable, blot out weak but ordinarily usable confirmatory bands or upset familiar intensity relationships. Finally, the functional group correlations are not always readily applied to structures in which the chromophore interacts strongly with substituent groups. The systems are often spatially compact, with functional groups so oriented that bonding or tautomerism seem inevitable.

Instruments

The infrared spectra of m-X and p-X dyes were recorded on Shimadzu Infrared Spectrometer double-beam recording spectrophotometer.

Sample Preparation

Infrared spectra of the dyes were obtained using solid samples in form of potassium bromide pellets. The color of m-X dye pellet is darker violet than the one of p-X dye. Both IR spectra were shown in Fig 3.1 and Fig 3.2.

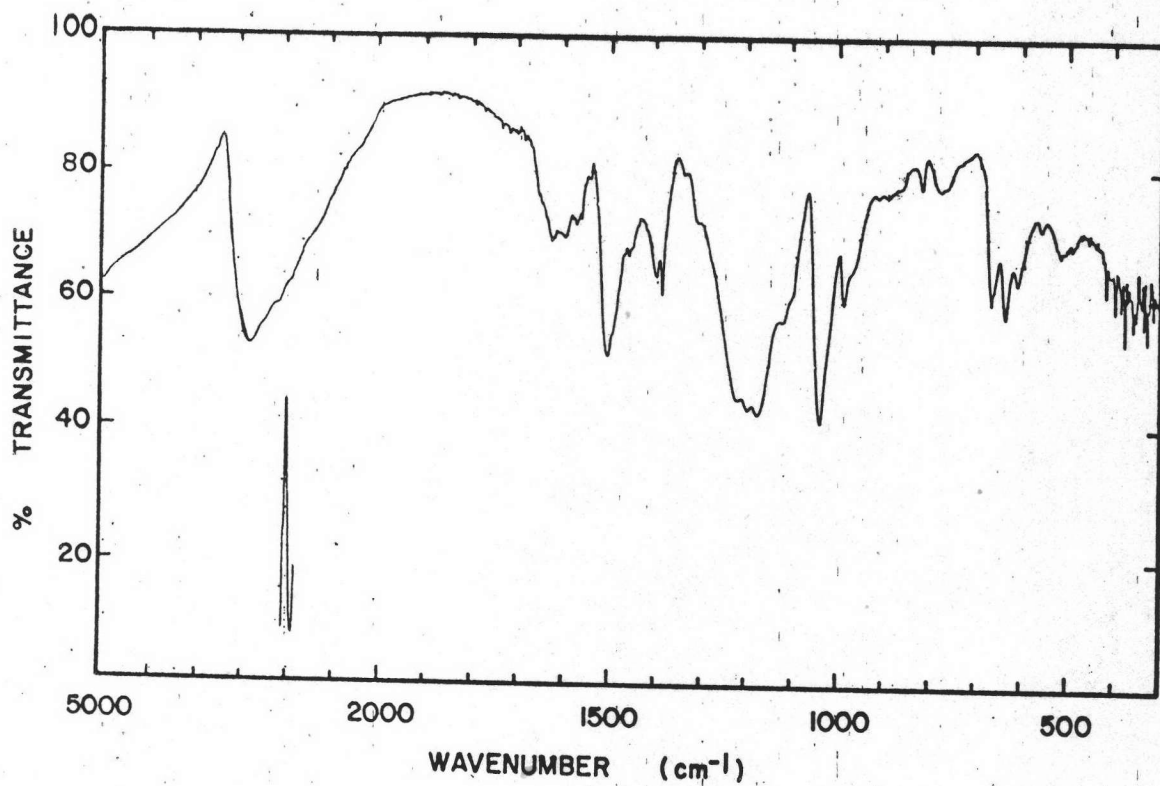


Fig 3.1 Infrared spectra of m-X dye.

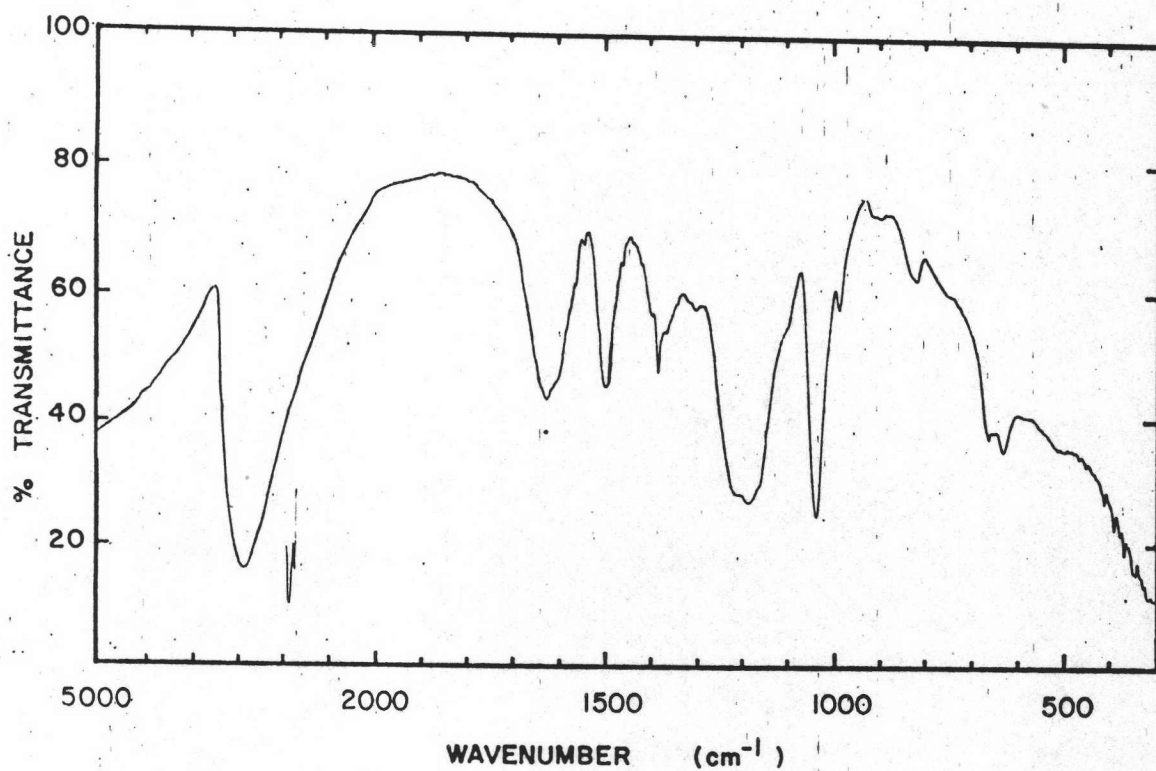


Fig 3.2 Infrared spectra of p-X dye.

The azo group (-N=N-) is very difficult to identify by infrared analysis (30). Infrared spectra of m-X and p-X dyes were very similar and difficult to clarify the difference between them. They showed strong absorptions in 3700-2000 cm^{-1} region and these could be due to -OH and -CH stretchings, but could also be partly due to moisture. A strong pattern in 1250-1000 cm^{-1} region, suggested the presence of the sulfonic acid groups. The spectrum of m-X dye showed more complex pattern in region 1680-1560 cm^{-1} than the one of p-X dye.

3.3 Nuclear Magnetic Resonance Spectroscopy of Synthetic Dyes

Nuclear magnetic resonance (NMR) spectroscopy is of great value in the structure elucidation of synthetic dyes (31). The ability of proton NMR (^1H NMR, PMR) to characterize aliphatic side chains and aromatic substitution patterns complements other spectrometric techniques such as IR. In addition, ^{13}C NMR (CMR) allows containing functional groups that have no attached protons (e.g., carbonyls, nitriles).

Analysis of dyes by NMR, however, presents some difficulties which, although not unique to this class of chemicals are more pronounced than for many other types of materials. Many dyes have moderately or highly complex structures and are sparingly soluble in NMR-compatible solvents. Also, occasionally, only a limited amount of

sample is available. Two relatively recent developments help the spectroscopist to cope with these problems : PMR at high magnetic fields, and Fourier transform (FT) NMR. The former provides greater chemical shift dispersion and higher sensitivity, and the latter not only facilitates the recording of PMR spectra of highly dilute solutions or of very small samples but also makes obtaining ^{13}C spectra a routine matter.

Instruments

Fourier transform NMR spectrometer FX90Q, (JEOL)

The PMR spectrum of m-X and p-X dyes in DMSO-d_6 solution indicated the presence of aromatic proton as shown in the Figures 3.3 and 3.4 respectively. In the case of PMR of p-X dye, it appeared that there were two aromatic proton peaks at 7.58 and 7.03. For m-X dye, three peaks of aromatic proton at 7.53, 7.39 and 7.11 were clearly identified and the complex patterns of aromatic proton also appeared in the range of 8.26 and 7.60. The appearance of these aromatic proton complex patterns are probably due to the fact that the p-X dye has more molecular symmetry in comparison with m-X dye. Results obtained from ^{13}C NMR of both m-X and p-X dye, in Figures 3.6 and 3.7 respectively, revealed that the numbers of peaks of p-X are less than those of m-X. This can also be explained in term of molecular symmetry which causes the superimposition of signals and less appearance of peak.

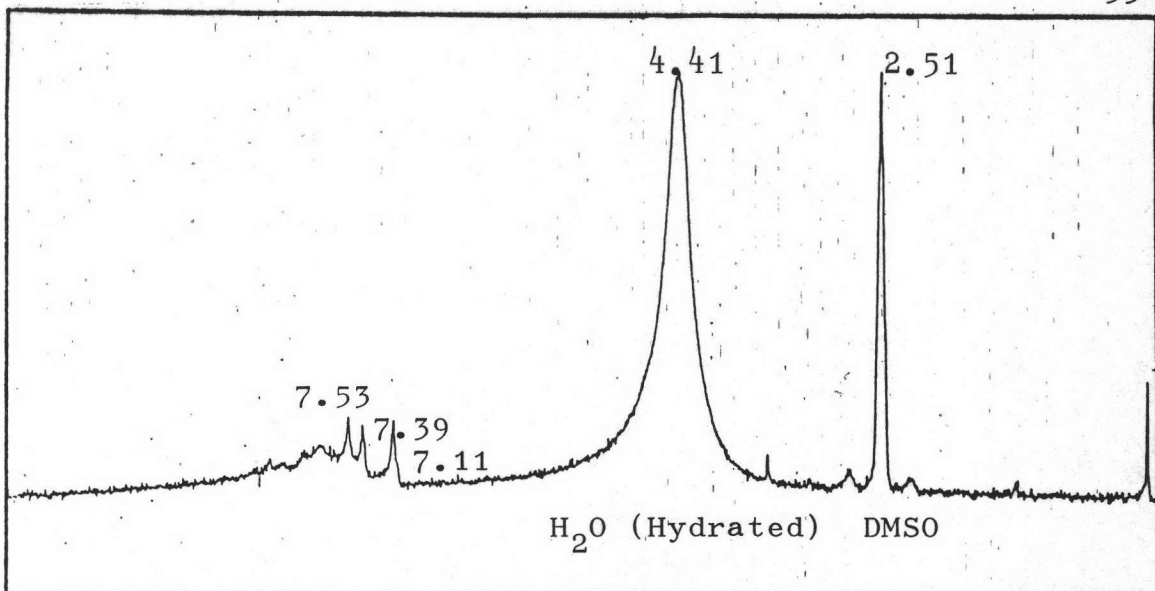


Fig.3.3 : ^1H NMR spectra of m-X dye.

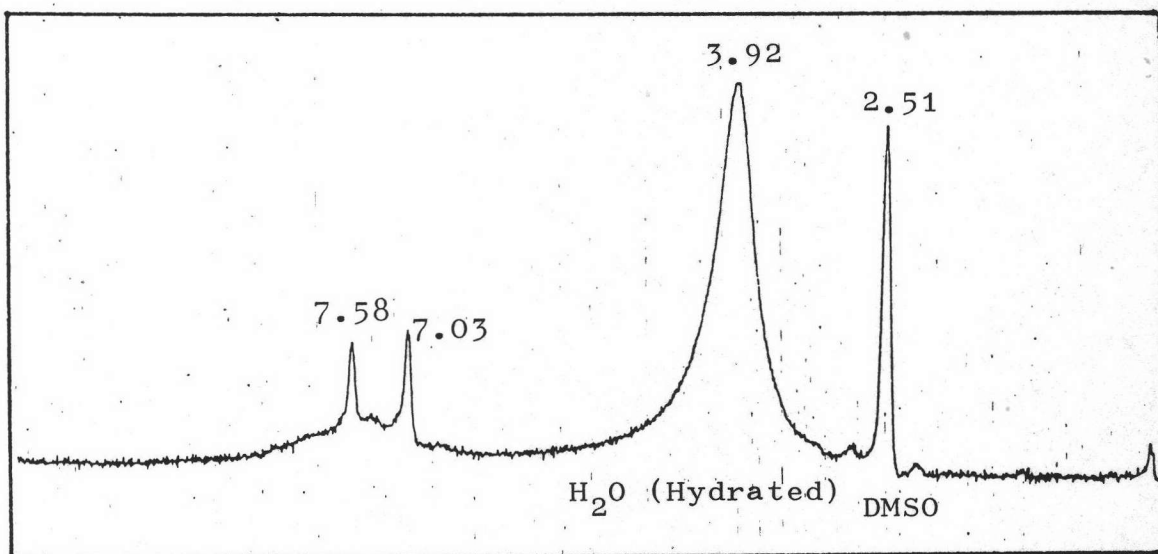


Fig.3.4 : ^1H NMR spectra of p-X dye.

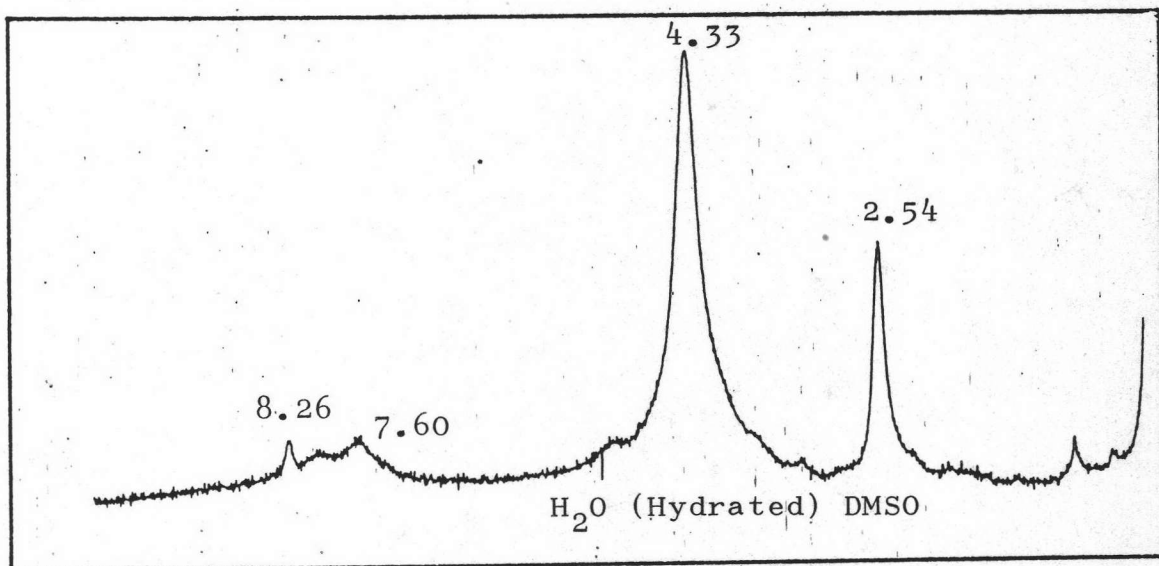


Fig.3.5 : ^1H NMR spectra of Chromotrope 2R.

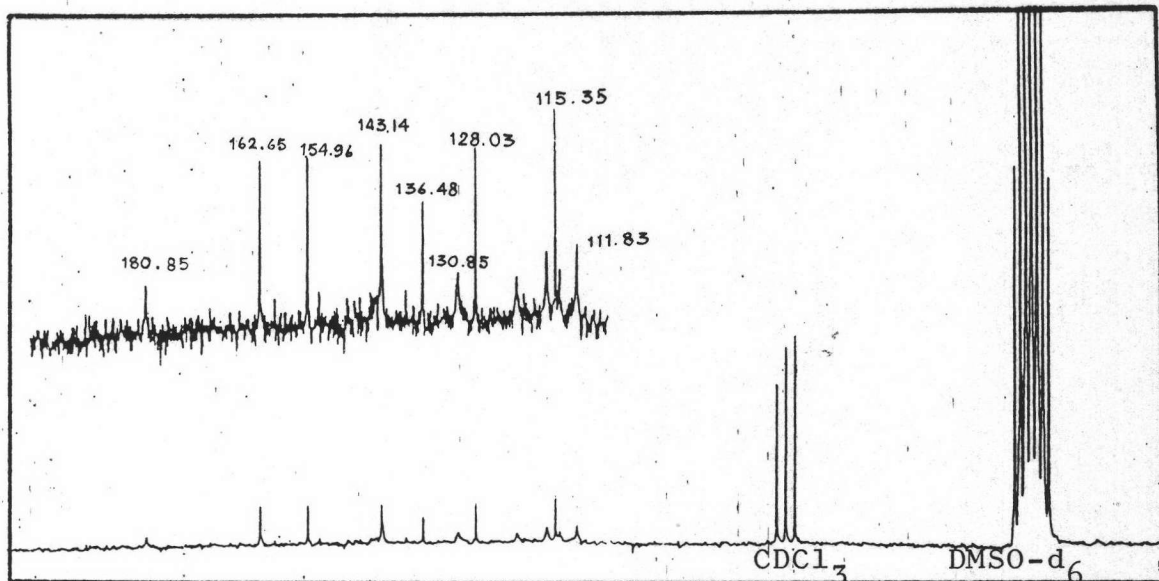


Fig.3.6 : ^{13}C NMR spectra of m-X dye.

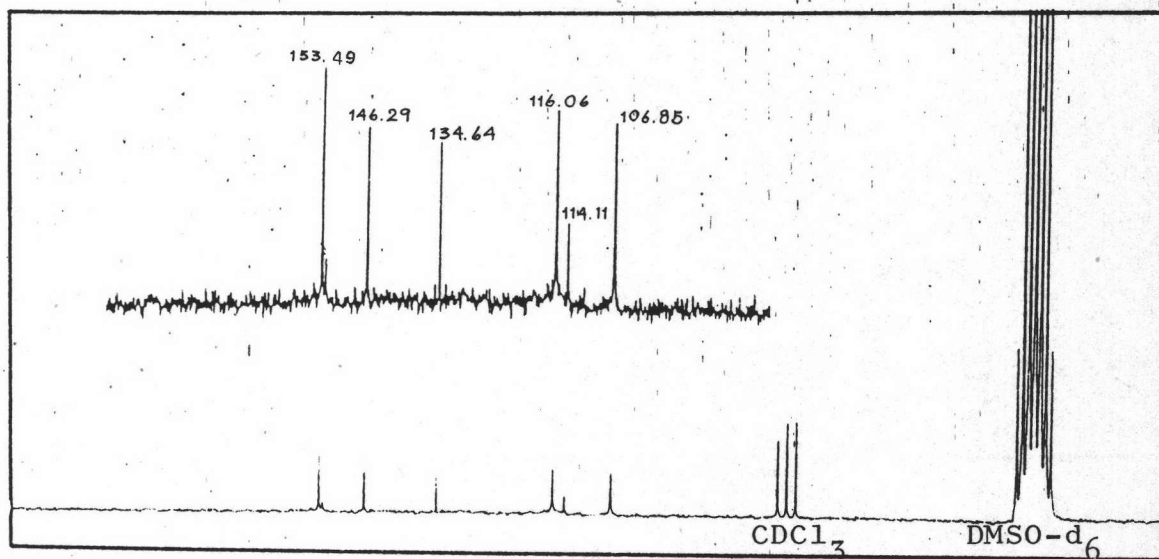


Fig.3.7 : ^{13}C NMR spectra of p-X dye.

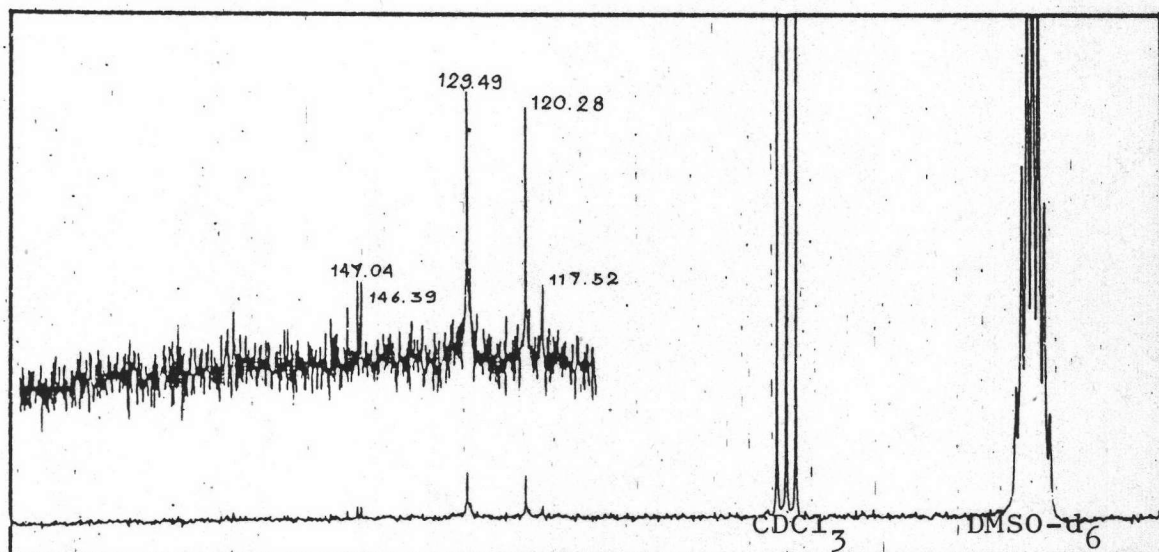


Fig.3.8 : ^{13}C NMR spectra of Chromotrope 2R.

In order to confirm that both m-X and p-X dyes being bis-azo compounds, ^1H and ^{13}C NMR spectra of a mono-azo compound which was previously synthesised by diazotizing aniline and then coupling with chromotropic acid were recorded as shown in Figures 3.5 and 3.8 compared with those of m-X and p-X dyes. It is seen that the spectra of mono-azo compound is completely different from those of m-X and p-X dyes.

3.4 Preliminary Studies of Metallochromic Property of m-X Dye and p-x Dye



Reagents

Dye solution : 0.5% w/v freshly prepared in water.

10^{-2} F Metal Solutions : Stock metal solutions were prepared by dissolving appropriate amounts of analytical grade of nitrate, chloride and sulfate salts of various metals.

10^{-2} F EDTA Solution : 0.932 g of ethylenediamine tetraacetic acid (disodium salt) was dissolved in deionized water and then diluted to 250 ml.

Solution for pH adjustment : Six solutions were prepared as follows:

| pH | Solutions |
|------|--|
| 2 | 2 F hydrochloric acid |
| 4 | acetate buffer (250 ml of glacial acetic acid + 137 g of sodium acetate trihydrate made up to 1 liter with distilled water) |
| 7 | sodium acetate trihydrate solution (20% w/v) |
| 10 | ammonia-ammonium chloride solution (NH_4Cl 70 g + NH_3 (sp.gr 0.880) 568 ml make up to 1 liter with distilled water) |
| 11.5 | ammonia solution (NH_3 sp.gr 0.880): distilled water = 1 : 1 |
| 12 | 2 F sodium hydroxide solution |

Procedure :

Preliminary studies of metallochromic property of the dye at pH 2-12 were carried out. Two series of the test tubes containing 1 ml of deionized water, 2 drops of dye solution and 2 drops of pH adjusting solution were placed on a test tube rack. To one series of the test tubes, was added 2 drops each, the solution of 10^{-2} F metal ions. The solution in each series was adjusted to pH 2, 4, 7, 10, 11.5, and 12 by pH adjusting solution listed in the above table. Color change due to the complex formation of metal ion with dye were observed and compared with the dye alone. 3 drops of 10^{-2} F EDTA was added into the test tube of metal-dye complex and any color change was then recorded.

The metallochromic properties of m-X dye and p-X dye at various pH values together with studie of EDTA as a mass masking agent are shown in Table 3.2 and Table 3.3 respectively.

Table 3.2 Visual color change studies of m-X Dye

| metal \ pH | 2 | 4 | 7 | 10 | 11.5 | 12 |
|----------------------|------------------|----------------|------------------|------------------|------------------|------------------|
| Dye(alone) | r | r | r | r | r | r |
| Ti(IV) | + | + | + | + | + | + |
| Cr(III) | + | + | + | v-r ^b | v-r ^b | v-r ^b |
| Mn(II) | + | + | + | r-v ^b | + | + |
| Fe(II) | + | + | + | + | + | + |
| Fe(III) | + | + | + | + | + | + |
| Co(II) | + | + | + | v ^b | r-v ^b | r-v ^b |
| Ni(II) | + | + | v ^b | v ^b | v ^b | ppt |
| Cu(II) | + | + | v ^b | v ^b | r-v ^b | r-v ^b |
| Zn(II) | + | + | + | + | + | + |
| Pb(II) | + | + | v-r ^b | v-r ^b | v-r ^b | v-r ^b |
| Cd(II) | + | + | + | + | + | + |
| W (VI) | + | + | + | + | + | + |
| Mo (VI) | + | + | + | + | + | + |
| Th (IV) | ppt ^a | v ^a | v ^b | ppt | ppt | ppt |
| UO ₂ (II) | v ^b | + | + | + | + | + |

Note

- + = no change ; v-r = violet-red
 r = red ; r-v = reddish-violet
 v = violet ; ppt = precipitated
 a = no change after the EDTA addition
 b = color change to the original dye color at the same pH.

Table 3.3 Visual color change studies of p-X Dye

| metal \ pH | 2 | 4 | 7 | 10 | 11.5 | 12 |
|----------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| Dye(alone) | v-r | v-r | v-r | v-r | v-r | v-r |
| Ti(IV) | + | + | + | + | + | + |
| Cr(III) | + | + | r-v ^b | r-v ^b | r-v ^b | r-v ^b |
| Mn(II) | + | + | + | + | + | + |
| Fe(II) | b-r ^b | b-r ^b | b-r ^b | + | + | + |
| Fe(III) | + | + | b-r ^b | + | + | + |
| Co(II) | + | + | + | + | + | + |
| Ni(II) | + | + | r-v ^b | v ^b | v ^b | ppt |
| Cu(II) | + | + | + | b-r ^b | b-r ^b | r-v |
| Zn(II) | + | + | + | + | + | + |
| Cd(II) | + | + | + | + | + | + |
| W(VI) | + | + | + | + | + | + |
| Mo(VI) | + | + | + | + | + | + |
| Th(IV) | v ^a | r-v ^a | r-v ^b | + | + | + |
| UO ₂ (II) | v ^b | + | + | + | + | + |

Note :

- + = no change ; v = violet
 v-r = violet-red ; b-r = brownish-red
 r-v = reddish-violet ; ppt = precipitated
 a = no change after the EDTA addition
 b = color change to the original dye color at the same pH.

3.5 Analytical Visible Spectrophotometric Studied of
1,3-bis(1,8-dihydroxy-3,6-disulfo-2-naphthylazo)-
benzene (m-X Dye).

Apparatus

Visible spectra were recorded with a UV-240 Shimadzu UV-Visible Recording Spectrophotometer, with 1 cm matched quartz cells. Measurements of pH were made with a pH meter (Radiometer Copenhagen, model PHM 63 Autocol equipped with a combined electrode). For all subsequent experiments, measurements were made by the use of the above apparatus.

Reagents

Stock m-X Dye solution : A 10^{-2} F dye was prepared by dissolving 0.8427 g of the purified dyestuff in 100 ml of deionized water. 10^{-3} F and 10^{-4} F of the dye solutions were prepared by further dilution of the 10^{-2} F dye solution. The solutions were kept in the absence of light in order to minimize the photochemical reaction of the dye.

Standard thorium solution : A standard thorium solution was prepared by dissolving 1.5159 g of thorium nitrate tetrahydrate (BDH) in deionized water, 1 ml of concentrated hydrochloric acid was also added to prevent possible hydrolysis and the solution was diluted to 250 ml with deionized water. The concentration of the solution was 0.01 F of thorium. This standard stock solution was then further diluted to the concentrations of 10^{-3} F with

deionized water. The 10^{-4} F solution was freshly prepared frequently to minimize the possible change in concentration due to the adsorption caused by the ionic exchange with the glass container etc. The concentration of the solution was occasionally checked by titration with EDTA using xylenol orange as indicator(25).

pH adjustments : Ammonia solution (10^{-2} F) and / or hydrochloric acid (10^{-2} F) were employed for pH adjustments of the solutions.

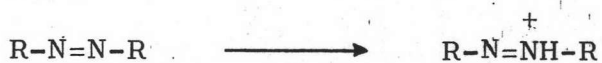
3.5.1. Acid-Base Property of m-X Dye

Twelve 2 ml aliquots of 10^{-4} F m-X dye solution were pipetted into a series of 100 ml beakers. The pH of the solution was adjusted to 1.0-12.0 by using nitric acid, ammonia solution or sodium hydroxide. Suitable amount of water was added. The pH of the solution was recorded by a pH meter. The solutions were then quantitatively transferred to a series of 50 ml volumetric flasks and made up to mark with deionized water. The color changes were observed and corresponding colors are reported in Table 3.4

The color of the free dye was found to change with pH. The change in color may be ascribed to change in the structure caused by ionization. The change in color when the pH was lowered is due to the attachment of a proton to the auxochromic groups or on one of the nitrogen atoms of the azo group and by increasing the pH, the process is reversed.

Table 3.4 Colors observed at particular pH values for m-X Dye.

| pH | Color observed |
|----|----------------|
| 1 | rosy red |
| 2 | rosy red |
| 3 | rosy red |
| 4 | rosy red |
| 5 | rosy red |
| 6 | rosy red |
| 7 | purple red |
| 8 | purple red |
| 9 | purple red |
| 10 | purple red |
| 11 | brownish red |
| 12 | brownish red |



The color changes resulted from Table 3.4 shows that m-X dye has acid-base property.

3.5.2 Visible Spectra of m-X Dye at Various pH values.

Procedure :

The previously prepared obtained from 3.5.1 were used for the spectra study. The absorption spectra of

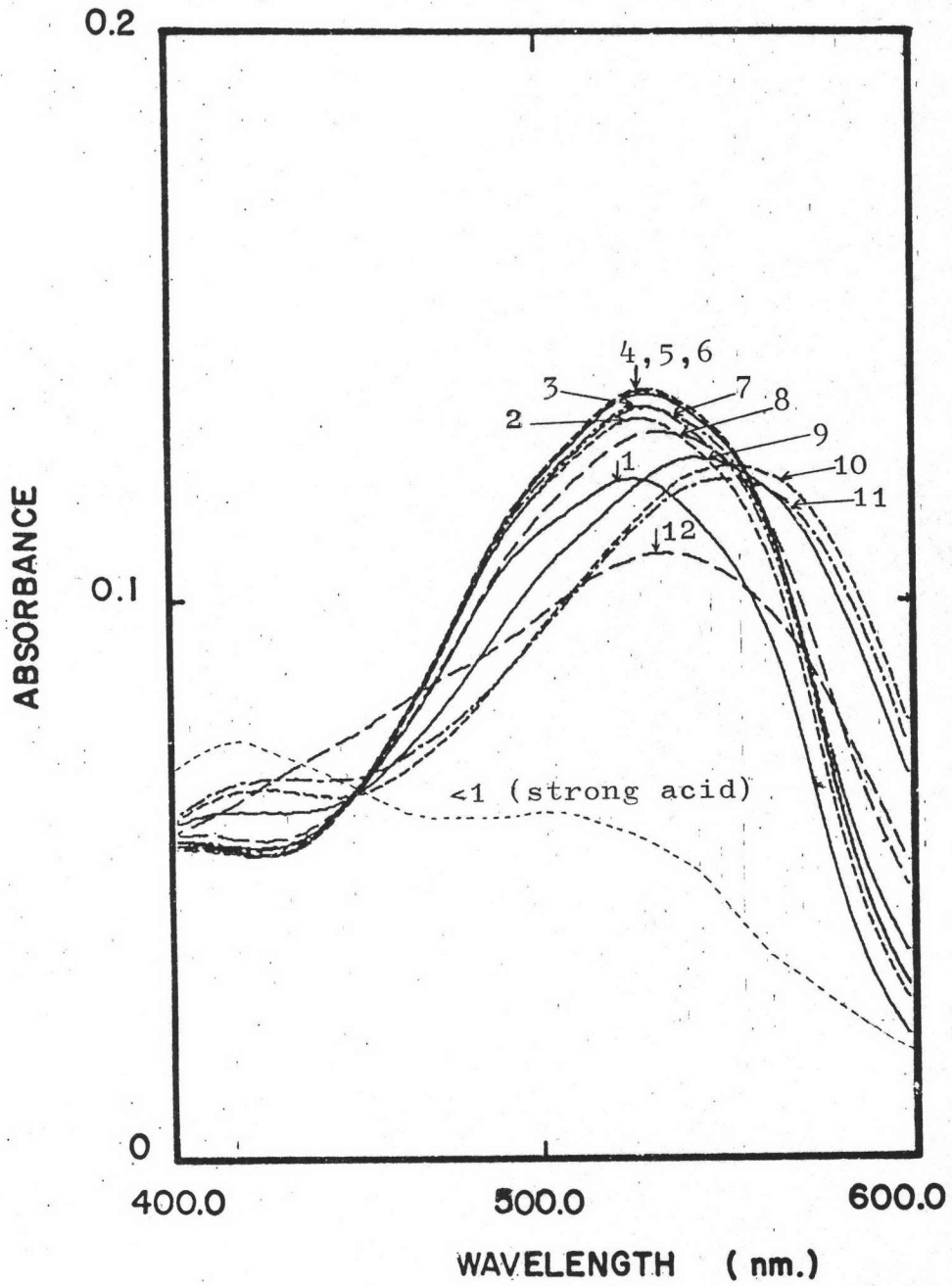


Fig 3.9 Absorption Spectra of the Dye at various pH (1-12).

m-X Dye : 10^{-4} F . 2 ml

Final volumn : 50 ml

Reference : Water

the dye solutions at various pH values were recorded from the wavelength of 400 nm to 600 nm using water as reference. The gain of the spectrophotometer was set at 0-0.2, the slit width was 2.0 nm.

The absorption spectra obtained are shown in Fig 3.9. The maximum absorbance occurs at about 527 nm over the pH range from 1.0 to 7.0, it shows a bathochromic shift above pH 7.0 and intensity of the color is decreased.

3.5.3 Visible Spectra of the Complex at Various pH.

The result from the qualitative color reaction indicates that the suitable pH range for complex formation is in the acid range.

Procedure :

Seven 3 ml aliquots of 10^{-2} F thorium were pipetted into a series of 100 ml beakers containing accurately 3 ml each of 10^{-4} F m-X dye solution. The pH of the solutions were adjusted to 2.0-5.0 with the interval of 0.5 by using nitric acid and ammonia solutions. The solutions were then quantitatively transferred into a series of 50 ml volumetric flasks. Small amount of water was added to the mark. The solutions were set aside for complete color development. The absorption spectra of the thorium-mX dye complex at pH 2.0-5.0 measured against water as a reference were recorded from 450-650 nm. The absorbance of the solutions were also measured against a reagent blank treated in a similar manner as a reference at 570-670 nm (in expanded scale) for easily observation.

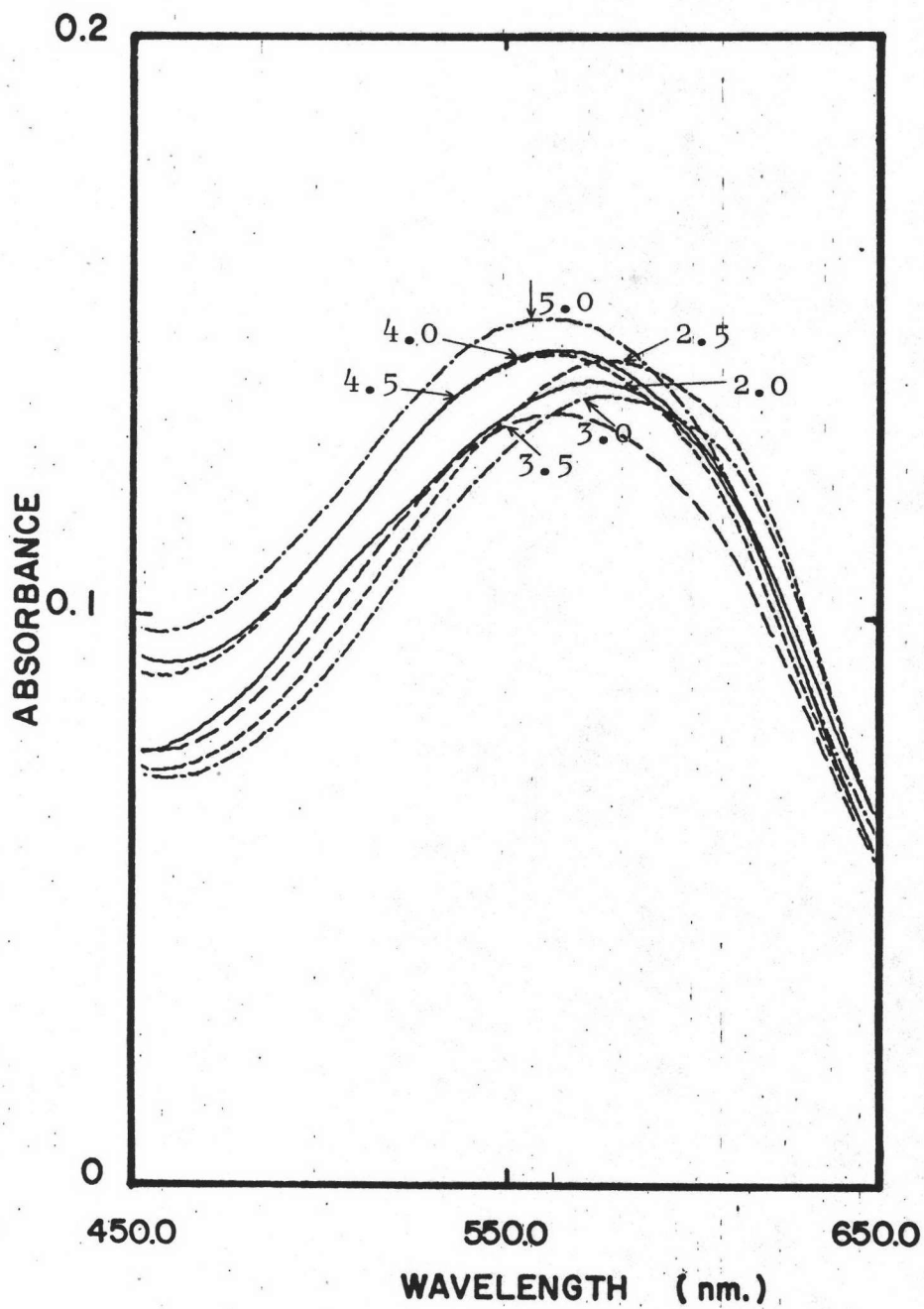


Fig.3.10 Absorption spectra of thorium - Dye complex at various pH (2.0-5.0).

Thorium : 10^{-2} F . 3 ml

m-X Dye : 10^{-4} F . 3 ml

Final volume : 50 ml

Reference : Water

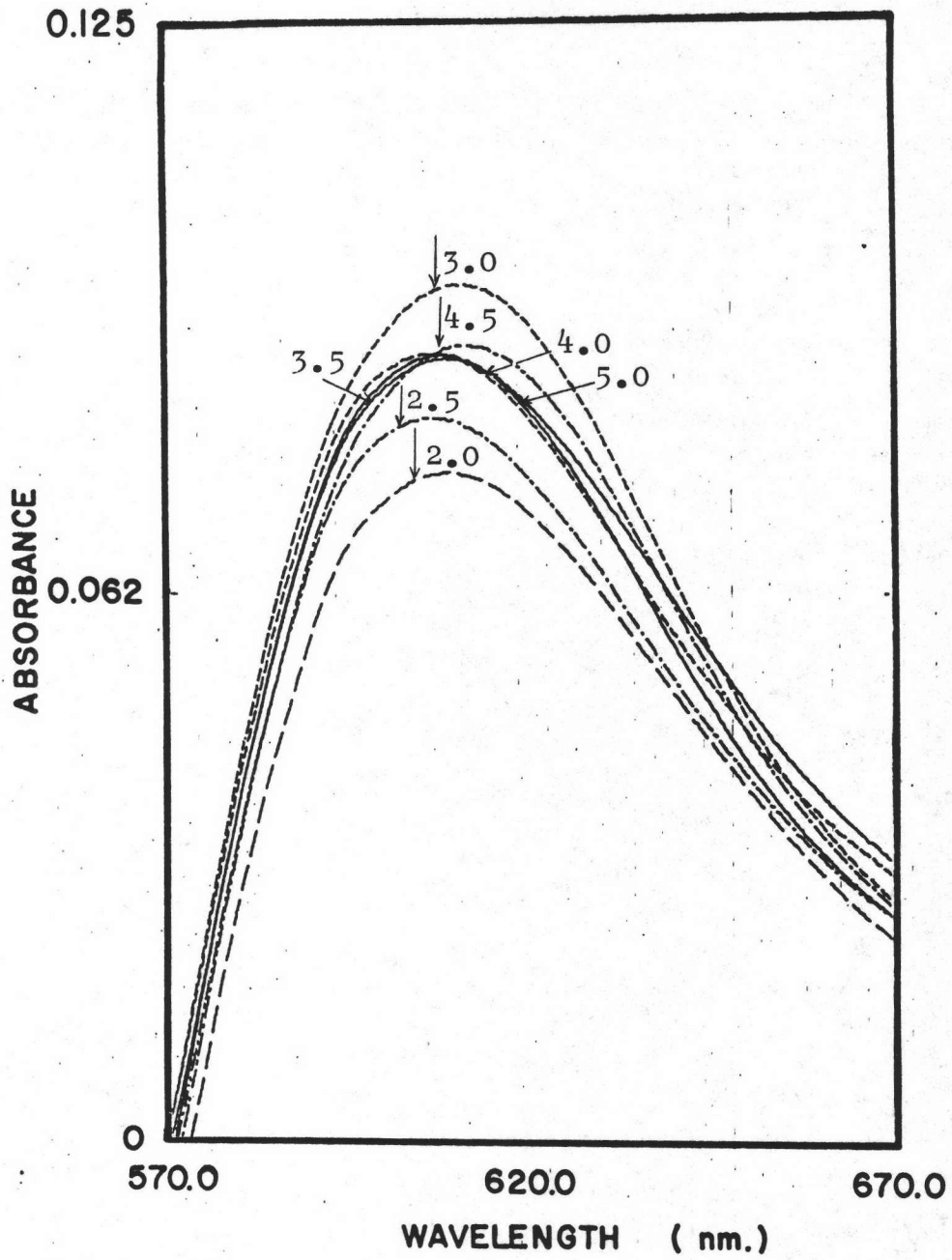


Fig.3.11 Absorption Spectra of Th. - Dye complex at various pH (2.0-5.0).

Thorium : 10^{-2} F . 3 ml

m-X Dye : 10^{-4} F . 3 ml

Final volume : 50 ml

Reference : Reagent blank

Figures 3.10 and 3.11 show the absorption spectra of the thorium - mX dye complex at various pH measured against water and reagent blank as references, respectively.

3.5.4 Spectrophotometric Determination of Thorium Using the m-X Dye as Metallochromic Reagents.

Experimental

Apparatus

The same set of instruments as previously described were used. The gain of the spectrophotometer was varied in each case but the slit width was fixed at 2.0.

Reagents

Standard thorium solution, 10^{-2} F. (as described previously)

Stock m-X Dye solution, 10^{-2} F. (as described previously)

Diverse ion solutions, 10^{-2} F. Stock solution of diverse ions were prepared from most analytical grade and some laboratory grade of various metal salts of nitrate, chloride and sulfate. Sodium salts were preferably employed in the case of anions. Dilute hydrochloric acid was added in these stock solutions whenever necessary. The concentrations were of 0.01 F, and further dilutions of these solutions were made when required. Deionized water was used in the preparation of all solutions.



Procedure:

In order to determine thorium spectrophotometrically using m-X dye as a reagent, the following conditions should be carefully studied and established:

- 1) Optimal wavelength for the thorium - mX dye complex.
- 2) Optimal pH
- 3) Sequence of addition
- 4) Optimal amount of m-X dye
- 5) Optimal time for color development

Optimal Conditions

Optimal Wavelength

Two set of solutions with different conditions, that is in one solution the excess of dye is used whereas the other the excess of metal is employed, were prepared for the investigation of the optimal analytical wavelength. The absorption spectra of the dye alone and the thorium-dye complex at pH 4 were recorded from 450-650 nm. The free dye was measured against water as a reference. The thorium-dye complex was measured against water and blank. The absorption spectra and experimental condition are shown in Fig 3.12

From the figure 3.12, at pH 4, m-X dye shows therefore, 610 nm was adopted as the analytical wavelength to be used throughout the subsequent experiments : the maximum absorption at 528 nm and the thorium-dye complex has maximum absorption at 610 nm.

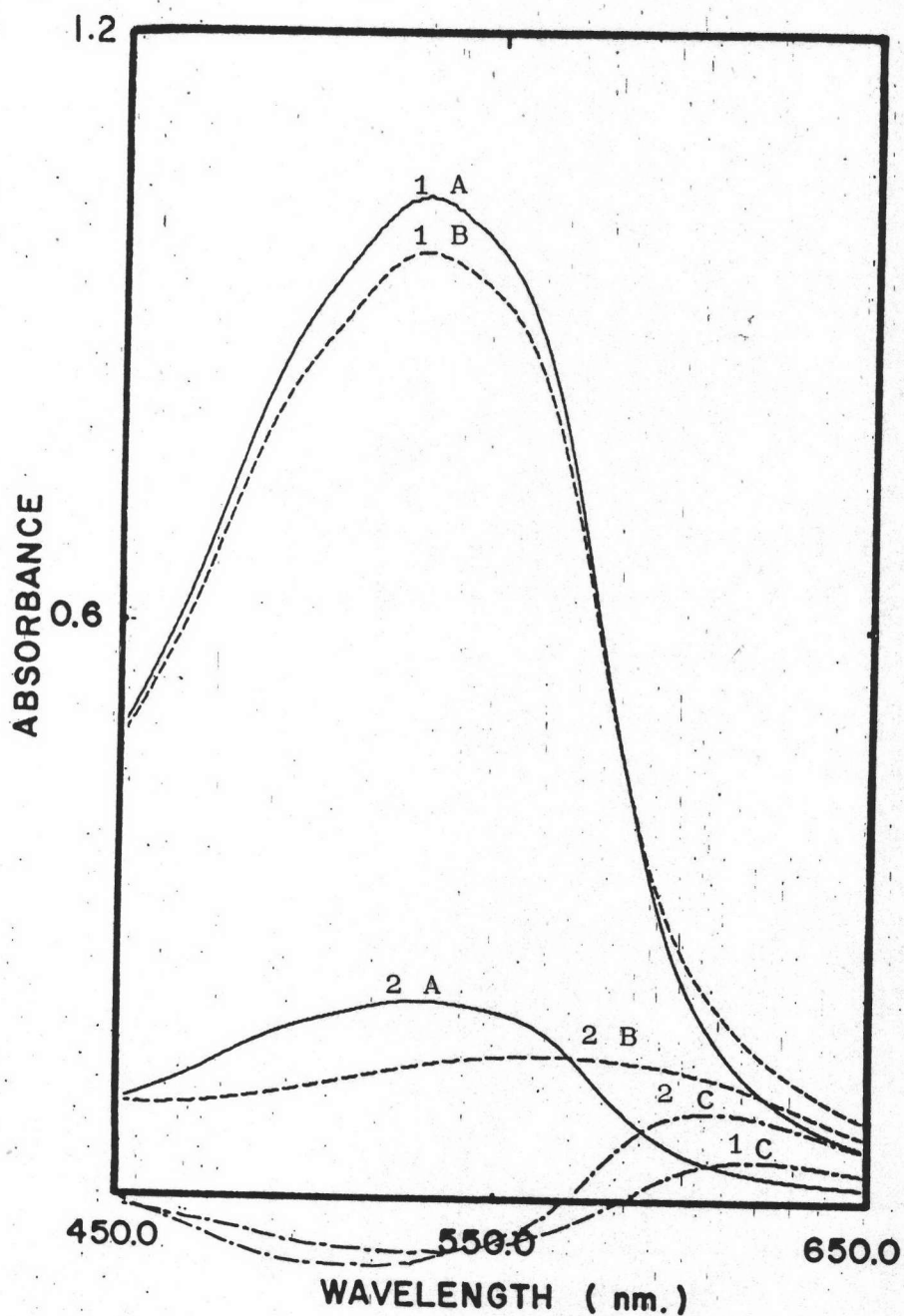


Fig.3.12 Optimal wavelength of the dye and its thorium complex at pH 4.0

- 1 A* : m-X Dye 10^{-3} F, 3 ml
 1 B* : m-X Dye 10^{-3} F, 3 ml and Th. 10^{-4} F, 3 ml
 1 C : 1 A against 1 B
 2 A* : m-X Dye 10^{-4} F, 3 ml
 2 B* : m-X Dye 10^{-4} F, 3 ml and Th. 10^{-3} F, 3 ml
 2 C : 2 A against 2 B

Final volumn : 50 ml

* : measure against water

Optimal pH

The effect of pH on the absorbance of the thorium-dye complex was investigated. A series of solutions containing 2 ml of 10^{-4} F thorium, 5 ml of 10^{-4} F m-X dye solution and appropriate amount of water was prepared. Nitric acid and ammonia solution were used for pH adjustment (between 2.0 and 7.0). The final volume was 50 ml. After the color was developed, the absorbances of solutions were measured at 610 nm against the reagent blank which was treated in a similar manner. The results obtained are shown in Table 3.5 and the corresponding plot appears in Fig 3.13.

It can be seen that the optimum pH range for analytical purpose lies in a narrow range between 3.5 and 4.5. Therefore, a pH of 4.0 was selected for all further work of this dye.

Sequence of Addition

The effect of the sequence of addition of all solutions concerned in the thorium - mX dye complex. Color development is shown in Table 3.6 and 3.7.

From the result above, it is rather clear that the order of addition of solutions shows no effect on the color development of thorium - mX dye complex. In practice, the sequence No. 2 was chosen for the subsequent experiments.

Table 3.5 : Optimal pH of thorium - mX dye complex.

| pH | Absorbance 610 nm |
|-----|----------------------|
| 2.0 | 0.027 |
| 2.5 | 0.037 |
| 3.0 | 0.046 |
| 3.5 | 0.050 |
| 4.0 | 0.051 |
| 4.5 | 0.050 |
| 5.0 | 0.049 |
| 6.0 | 0.023 |

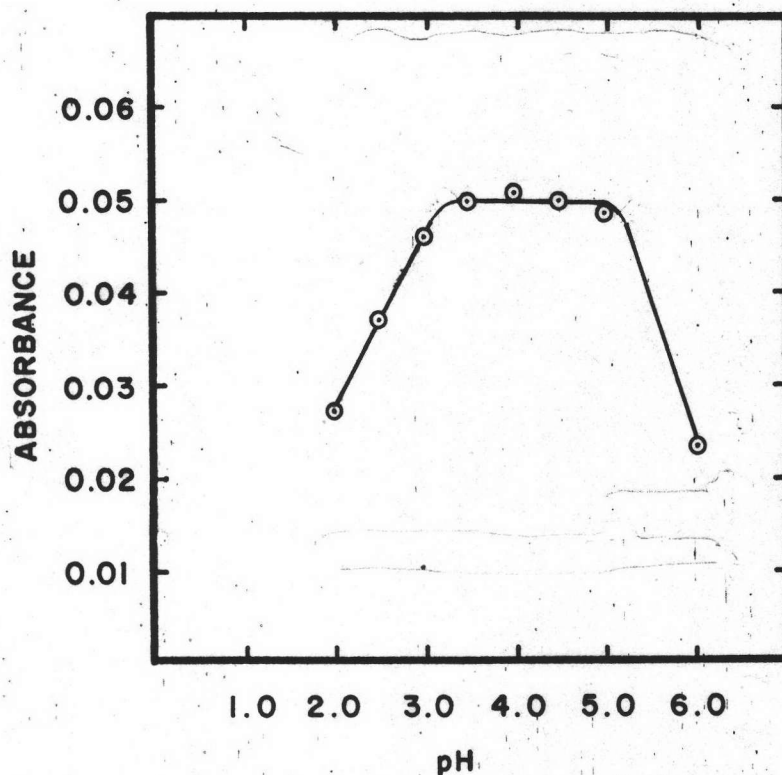


Fig.3.13 Effect of pH on absorbance of thorium-mX dye complex measured against a reagent blank at 610 nm
 m-X Dye : 10^{-4} F 5 ml ; Th. : 10^{-4} F 2 ml
 Final volume: 50 ml

Table 3.6 : Sequence of addition.

| Sequence No. | Sequence of reagent addition |
|--------------|--|
| 1 | dye, metal, pH adjustment, dilution |
| 2 | dye, metal, water, pH adjustment, dilution |
| 3 | dye, water, pH adjustment, metal, dilution |
| 4 | dye, pH adjustment, metal, dilution |
| 5 | metal, pH adjustment, dye, dilution |
| 6 | metal, water, pH adjustment, dye, dilution |

Table 3.7 : Absorbance of solutions from Table 3.6

| Sequence No. | Absorbance at 610 nm (against blank) |
|--------------|---|
| 1 | 0.048 |
| 2 | 0.050 |
| 3 | 0.050 |
| 4 | 0.049 |
| 5 | 0.050 |
| 6 | 0.050 |

Note

m-X Dye : 5 ml of 10^{-4} F.

Thorium : 2 ml of 10^{-4} F.

Final volumn : 50 ml

pH : 4



Optimal Amount of the Dye

The effect of the amount of the dye on the absorbance of the thorium - dye complex system was studied by varying the molar ratio of the reagent to thorium. The amount of metal was kept constant. A series of solutions containing 2 ml of 10^{-4} F. thorium, with various amount of 10^{-4} F dye solution from 1 to 10 ml and appropriate amount of water were prepared. The pH of each solution was adjusted to 4.0 by the addition of 0.01 N nitric acid or 0.01 N ammonia solution. Each content was then quantitatively transferred and diluted to a 50 ml volumetric flask. The absorbance of each solution was measured at 610 nm against the reagent blank using 1 cm cells.

The absorbance of solutions containing various ratio of dye to thorium at pH value of 4.0 are shown in Table 3.8 and the corresponding plot appears in Fig 3.14

The results in Fig 3.14 show that the absorbance increases with increasing amount of dye reagent up to 2 ml and then remains reasonably constant up to 10 ml. Therefore in this system, 5 ml of 10^{-4} F. dye was adopted to be used in the subsequent experiments.

Optimal time for color development

3 ml of 10^{-4} F thorium solution was pipetted into a 50 ml volumetric flask containing exactly 5 ml of 10^{-4} F. m-X dye solution. 0.2 ml of 0.1 F ammonia solution was added into the thorium - dye solution whereas 0.6 ml of

Table 3.8 : Optimal amount of m-X dye.

| Th. 10^{-4} F (ml) | m-X Dye 10^{-4} F (ml) | Absorbance 610 nm |
|-------------------------|-----------------------------|----------------------|
| 2 | 1 | 0.025 |
| 2 | 2 | 0.052 |
| 2 | 3 | 0.053 |
| 2 | 4 | 0.053 |
| 2 | 5 | 0.052 |
| 2 | 6 | 0.054 |
| 2 | 7 | 0.054 |
| 2 | 8 | 0.055 |
| 2 | 9 | 0.050 |
| 2 | 10 | 0.050 |

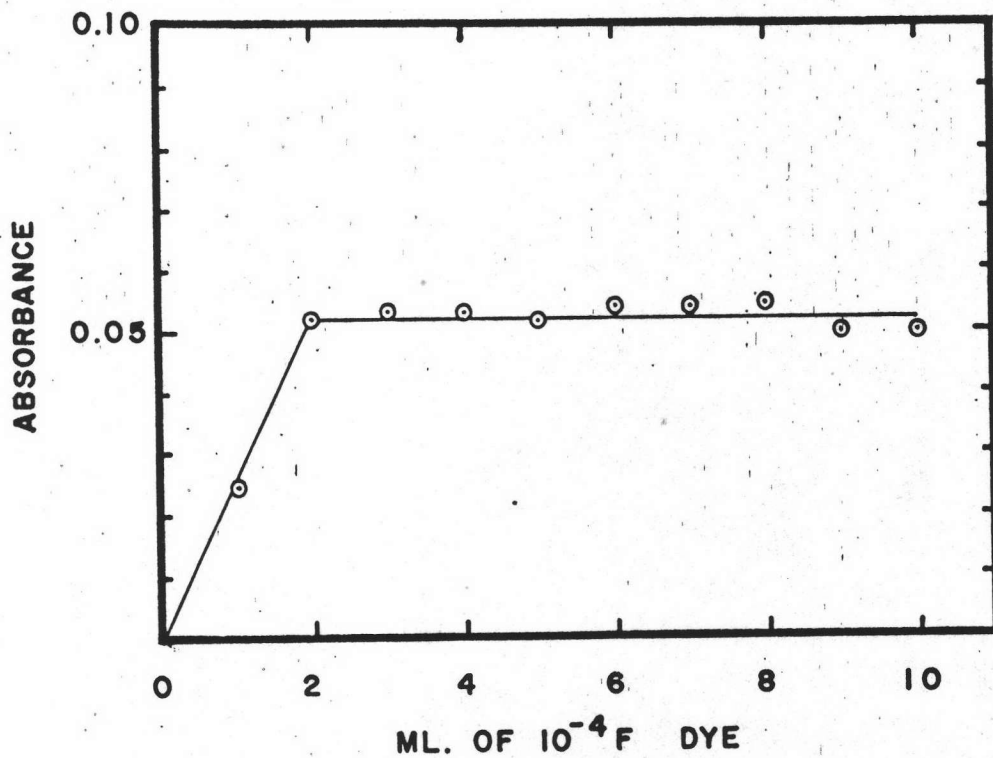


Fig.3.14 : Effect of reagent concentration.

Thorium : 10^{-4} F . 2 ml

Final volumn : 50 ml

Reference : Reagent blank

Table 3.9: Effect of time on color development of the complex.

| Time | Absorbance 610 nm | Time | Absorbance 610 nm |
|----------|----------------------|---------|----------------------|
| 0 minute | 0.081 | 2 hours | 0.080 |
| 1 " | 0.081 | 4 " | 0.080 |
| 2 " | 0.082 | 6 " | 0.081 |
| 5 " | 0.081 | 8 " | 0.081 |
| 8 " | 0.081 | 10 " | 0.081 |
| 10 " | 0.081 | 12 " | 0.080 |
| 15 " | 0.081 | 18 " | 0.080 |
| 20 " | 0.080 | 24 " | 0.080 |
| 25 " | 0.080 | 30 " | 0.080 |
| 30 " | 0.082 | 36 " | 0.080 |
| 45 " | 0.081 | 40 " | 0.080 |
| 60 " | 0.081 | 48 " | 0.080 |

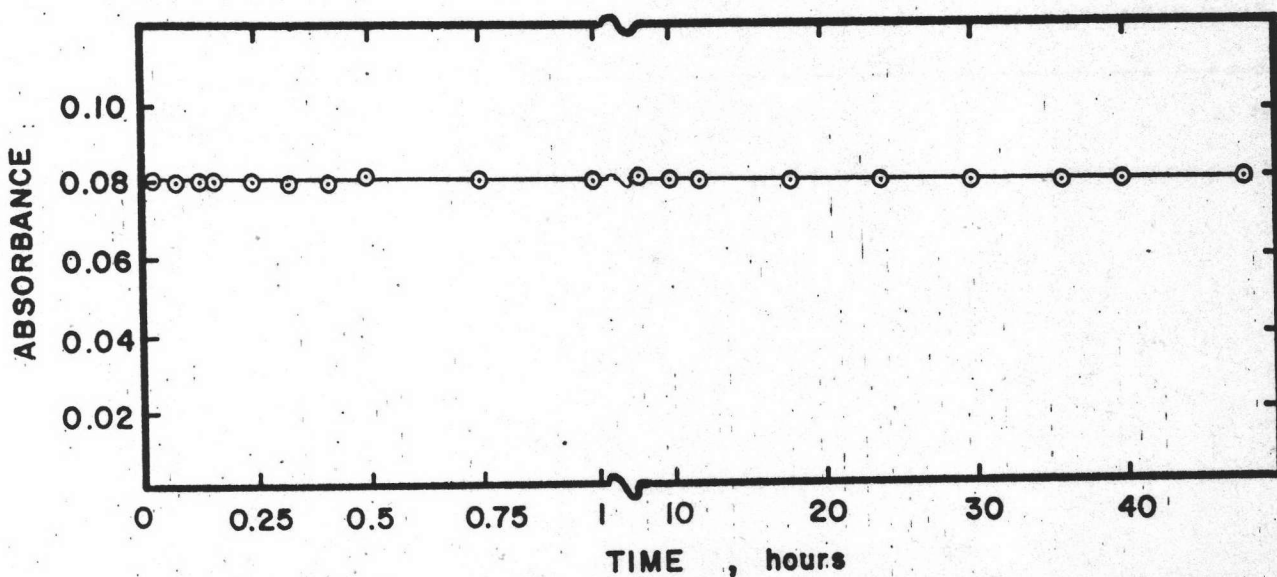


Fig. 3.15: The influence of time on the absorbance of the thorium - mX dye complex.

0.01 N nitric acid was added into the reagent blank for adjusting pH to 4.0. Both solutions were then made up to 50 ml. mark with deionized water. The absorbance of the thorium-dye solution was measured immediately after dilution against a reagent blank at 610 nm, using 1 cm cells. The absorbance of the thorium-dye complex solution was then measured periodically at the specified time intervals. Results are shown in Table 3.9 and corresponding Fig 3.15.

Result obtained shows that the color of the complex is developed instantaneously and remains constant for at least 48 hours.

Adherence to Beer-Bouguer-Lambert Law

Calibration Curve

The linearity relationship between the absorbance of the thorium - mX dye complex and the thorium concentrations was investigated. In this study, 0 to 10 ml of 10^{-4} F thorium solutions were pipetted into a series of 100 ml beakers containing 5 ml of 10^{-4} F dye solution and appropriate amount of water. The pH of solution was then adjusted to 4.0 by using 0.01 F nitric acid or 0.01 F ammonia solution. The solutions were then quantitatively transferred to a series of 50 ml volumetric flasks. Small amount of deionized water was added to adjust the mask. The absorbances of these solutions were measured at 610 nm against the reagent blank using 1 cm cells. The data

obtained is shown in Table 3.10 and corresponding plot in Fig 3.16.

The calibration curve is found to obey Beer-Bouguer-Lambert Law very well over the range of 2.3 to 116 μg of thorium in 50 ml of solution at 610 nm. The molar absorptivity coefficient (ϵ) is $1.31 \times 10^4 \text{ l.mol}^{-1}.\text{cm}^{-1}$, equivalent to the specific absorptivity (a) of $0.06 \text{ ml.g}^{-1}.\text{cm}^{-1}$ and the sandell sensitivity (S) of $0.0177 \mu\text{g}.\text{cm}^{-2}$.

Table 3.10 : Calibration curve of thorium - mX dye complex

| m-X Dye 10^{-4} F (ml) | Th. 10^{-4} F | | Absorbance 610 nm |
|-----------------------------|-----------------|----------|----------------------|
| | (ml) | g/50 ml. | |
| 5 | 0.1 | 2.3038 | 0.005 |
| 5 | 0.2 | 4.6408 | 0.009 |
| 5 | 0.5 | 11.6019 | 0.013 |
| 5 | 1.0 | 23.2038 | 0.028 |
| 5 | 1.5 | 34.8057 | 0.039 |
| 5 | 2.0 | 46.4076 | 0.054 |
| 5 | 2.5 | 58.0095 | 0.069 |
| 5 | 3.0 | 69.6114 | 0.086 |
| 5 | 3.5 | 81.2133 | 0.099 |
| 5 | 4.0 | 92.8152 | 0.110 |
| 5 | 4.5 | 104.4171 | 0.119 |
| 5 | 5.0 | 116.0190 | 0.130 |
| 5 | 6.0 | 139.2228 | 0.139 |
| 5 | 7.0 | 162.4266 | 0.141 |
| 5 | 8.0 | 185.6304 | 0.146 |
| 5 | 9.0 | 208.8342 | 0.146 |
| 5 | 10.0 | 232.0381 | 0.146 |

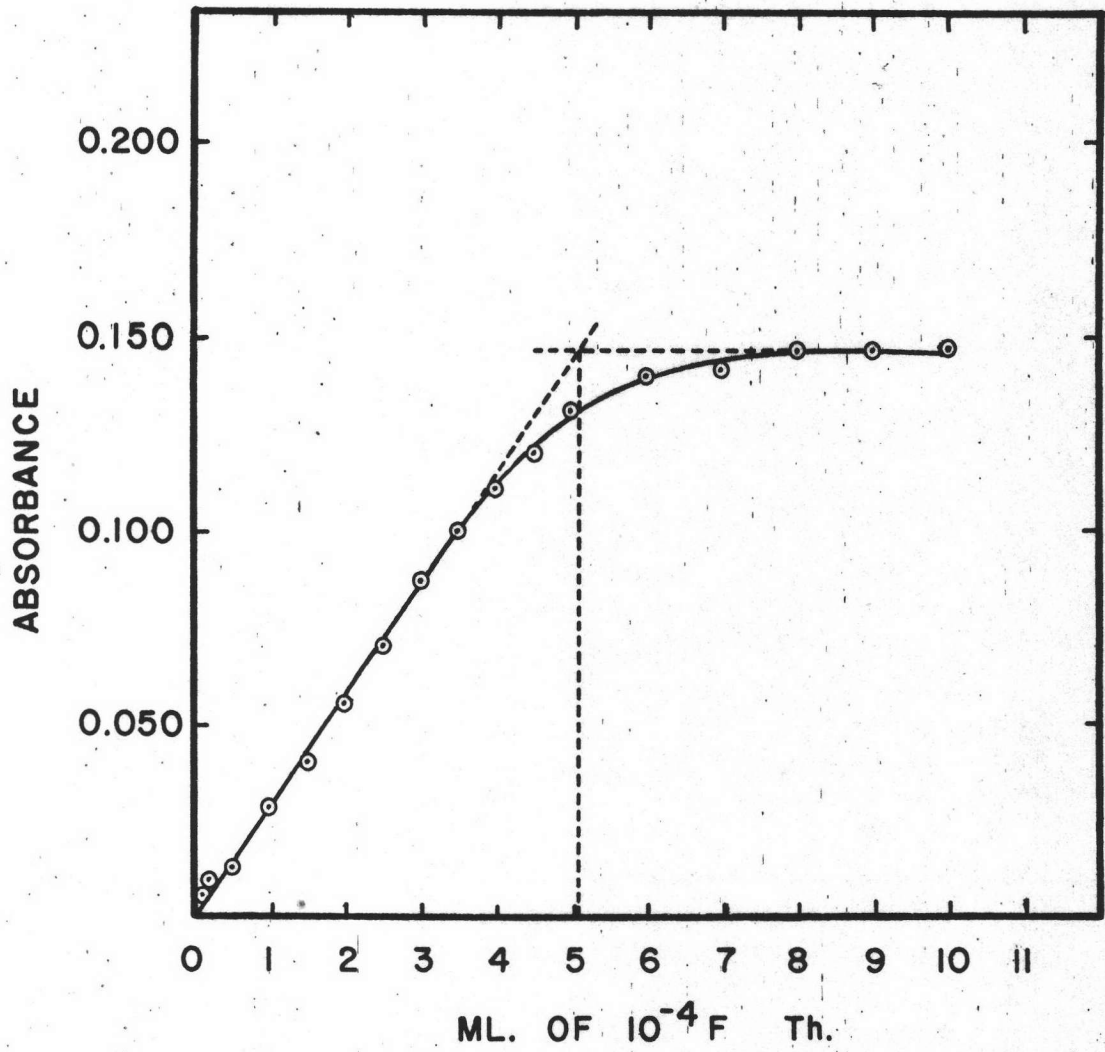


Fig. 3.16: Calibration Curve of thorium - mX dye complex.

Reproducibility of the method

The reproducibility of this method was checked by means of the standard deviation of the determination obtained from measuring the absorbance of 10 sets of solution, each containing 5 ml of 10^{-4} F dye solution, 3 ml of 10^{-4} F thorium and appropriate amount of water under the optimal conditions. The data obtained is reported in Table 3.11.

The standard deviation, s , was calculated using the formula:

$$s = \pm \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}}$$

where x = individual value
 \bar{x} = mean value
 n = number of value

Table 3.11: Standard deviation study of the method

| Dye 10^{-4} F (ml) | Th. 10^{-4} F (ml) | Absorbance at 610 nm. |
|-------------------------|-------------------------|--------------------------|
| 5 | 3 | 0.082 |
| 5 | 3 | 0.080 |
| 5 | 3 | 0.081 |
| 5 | 3 | 0.082 |
| 5 | 3 | 0.081 |
| 5 | 3 | 0.084 |
| 5 | 3 | 0.080 |
| 5 | 3 | 0.081 |
| 5 | 3 | 0.082 |
| 5 | 3 | 0.082 |

$$\bar{X} = 0.082$$

$$n = 10$$

$$s = \pm 0.001$$

$$\therefore \text{Percent standard deviation} = \pm 0.1$$

Effect of diverse ions

The effect of 21 cations and 9 anions on the determination of thorium was examined in various concentrations.

A series of solutions containing 3 ml of 10^{-4} F thorium, 5 ml of 10^{-4} F m-X dye solution with various mole ratios of the diverse ions to thorium (100 : 1 , 50 : 1, 10 : 1 and 1 : 1) were prepared using 3 ml, 1.5 ml of 10^{-2} F, 3 ml of 10^{-3} F and 3 ml of 10^{-4} F diverse ions solutions.

These diverse ions were added individually to a thorium-dye solution. The pH of the solutions were adjust to 4.0 by 0.01 F nitric acid and 0.01 F ammonia solution. The final volume was 50 ml.

The absorbance of the solutions were measured at 610 nm against a reagent blank using 1 cm cell. The results obtained are summarized in Tables 3.12 and 3.13.

Table 3.12: Effect of some cations

| condition | Absorbance at 610 nm | | | |
|------------------------|----------------------|-------------|-------------|--------------|
| | Th:ion=1:1 | Th:ion=1:10 | Th:ion=1:50 | Th:ion=1:100 |
| Th. alone | 0.080 | 0.080 | 0.080 | 0.080 |
| + Mg(II) | 0.082 | 0.085 | 0.087 | 0.089 |
| + Ba(II) | 0.084 | 0.092 | 0.092 | 0.093 |
| + Ti(IV) | 0.079 | 0.060 | ppt | ppt |
| + V(V) | 0.058 | 0.029 | 0.018 | 0.000 |
| + Cr(III) | 0.081 | 0.081 | 0.074 | 0.070 |
| + Mn(II) | 0.081 | 0.079 | 0.075 | 0.066 |
| + Fe(II) | 0.088 | 0.079 | 0.076 | 0.094 |
| + Fe(III) | 0.083 | ppt | ppt | ppt |
| + Co(II) | 0.080 | 0.080 | 0.080 | 0.083 |
| + Ni(II) | 0.078 | 0.079 | 0.081 | 0.085 |
| + Cu(II) | 0.079 | 0.086 | 0.097 | 0.102 |
| + Zn(II) | 0.080 | 0.081 | 0.081 | 0.081 |
| + Pb(II) | 0.080 | 0.076 | 0.087 | 0.089 |
| + Cd(II) | 0.080 | 0.080 | 0.081 | 0.083 |
| + Sn(II) | 0.061 | 0.100 | ppt | ppt |
| + Sr(II) | 0.080 | 0.082 | 0.087 | 0.091 |
| + Ag(I) | 0.081 | 0.084 | 0.084 | 0.084 |
| + Mo(VI) | 0.081 | 0.084 | 0.089 | 0.091 |
| + W(VI) | 0.081 | 0.083 | 0.086 | 0.087 |
| + Ce(IV) | 0.084 | 0.096 | ppt | ppt |
| + UO ₂ (II) | 0.088 | 0.096 | 0.140 | 0.150 |

Table 3.13: Effect of some anions

| condition | Absorbance at 610 nm | | | |
|---------------------------------|----------------------|-------------|-------------|--------------|
| | Th:ion=1:1 | Th:ion=1:10 | Th:ion=1:50 | Th:ion=1:100 |
| Th. alone | 0.080 | 0.080 | 0.080 | 0.080 |
| + citrate | 0.071 | 0.059 | 0.049 | 0.048 |
| + oxalate | 0.077 | 0.054 | 0.048 | 0.048 |
| + EDTA | 0.062 | 0.047 | 0.047 | 0.047 |
| + Cl ⁻ | 0.080 | 0.080 | 0.082 | 0.082 |
| + F ⁻ | 0.074 | 0.072 | 0.044 | 0.040 |
| + SO ₄ ²⁻ | 0.080 | 0.078 | 0.078 | 0.078 |
| + acetate | 0.080 | 0.078 | 0.076 | 0.074 |
| + CO ₃ ²⁻ | 0.080 | 0.080 | 0.080 | 0.080 |
| + PO ₄ ³⁻ | 0.080 | 0.078 | 0.078 | 0.076 |

It can be concluded from Table 3.11 and Table 3.12 , based on the deviation of $\pm 5\%$ from the standard sample (without diverse ions) that V(V), Fe(III), Sn(II), Ce(IV), UO₂(II), EDTA, citrate, oxalate, F⁻ interfere seriously when the interfering ion present in the amount of 100 moles excess over that of thorium and the effect is decreased as the amount of the diverse ion decreases; the following ions namely, Co(II), Zn(II), Cd(II), Ag(I), Cl⁻, CO₃²⁻, SO₄²⁻ do not interfere within the 100 moles excess. If the ratio of the interfering ion to thorium is reduced to 50, Ni(II) does not interfere and Cr(III), Mn(II), Fe(II), Sr(II) do

not interfere if the ratio is 10, and Mg(II), Ba(II), Cu(II), Pb(II), Mo(VI), W(VI), PO_4^{3-} do not interfere if the ratio is equal to 1.

3.5.5 Determination of Empirical Formula of the Complex

3.5.5.1 Method of Continuous Variation (Job's Method)

Procedure :

A series of solution of thorium - mX dye mixtures containing various mole fractions of thorium from 0-1 was prepared. The sum of the concentrations of thorium and the dye was kept constant at 0.1×10^{-5} mole per liter. After adjustment pH to 4.00, mixtures were diluted to 100 ml. The absorbance of each solution was measured at 610 nm against water as the reference using 1 cm cell. The data is shown in Table 3.14 and the corresponding Job's plot is shown in Fig.3.17.

From the Fig.3.17, it shows that a 1 : 1 mole ratio complex is formed between thorium and the dye.

The apparent stability constant of the thorium - mX dye complex under the conditions of this experiment was evaluated. On the basis of the previous experiments, a 1 : 1 metal-ligand complex is assumed,



it is possible to write the stability constant as;

$$K = \frac{(1 - \alpha)}{\alpha^2 C}$$

where α , the degree of dissociation, was established from the relationship:

$$\alpha = \frac{A_m - A_s}{A_m}$$

and C is the concentration of the complex in mole per liter.

The continuous variation curve (Fig 3.17) may be used to obtain the values of A_m and A_s . From Fig 3.17, it was found that A_m is equal to 0.063 and A_s is equal to 0.060 for a solution that was 10^{-5} M. in thorium. The degree of dissociation constant was calculated to be 0.048. The value of the apparent stability constant, K, under these particular conditions was found to be 4.1×10^7 with the pK values of 7.61. This value indicates that at pH 4.0 the complex-formation between Th(IV) and m-X dye is rather strong and stable.

3.5.5.2 The Mole Ratio Method

Procedure :

A series of solutions containing equal formal concentration of the dye but different formal concentrations of thorium were prepared. The concentration of dye was fixed at 0.1×10^{-4} mole/liter (5 ml of 10^{-4} F m-X dye solution per 50 ml) with variation of 10^{-4} F thorium 0-10 ml. The pH of

Table 3.14: The detailed data of the method of continuous variation. (Job's method).

| Dye 10^{-4} F (ml) | Th 10^{-4} F (ml) | mole fraction of thorium Th/Th+m-x dye | Absorbance at 610 nm |
|----------------------|---------------------|--|----------------------|
| 10 | 0 | 0.0 | 0.0596 |
| 9 | 1 | 0.1 | 0.0636 |
| 8 | 2 | 0.2 | 0.0716 |
| 7 | 3 | 0.3 | 0.0776 |
| 6 | 4 | 0.4 | 0.0826 |
| 5 | 5 | 0.5 | 0.0886 |
| 4 | 6 | 0.6 | 0.0756 |
| 3 | 7 | 0.7 | 0.0586 |
| 2 | 8 | 0.8 | 0.0386 |
| 1 | 9 | 0.9 | 0.0196 |
| 0 | 10 | 1.0 | 0.0000 |

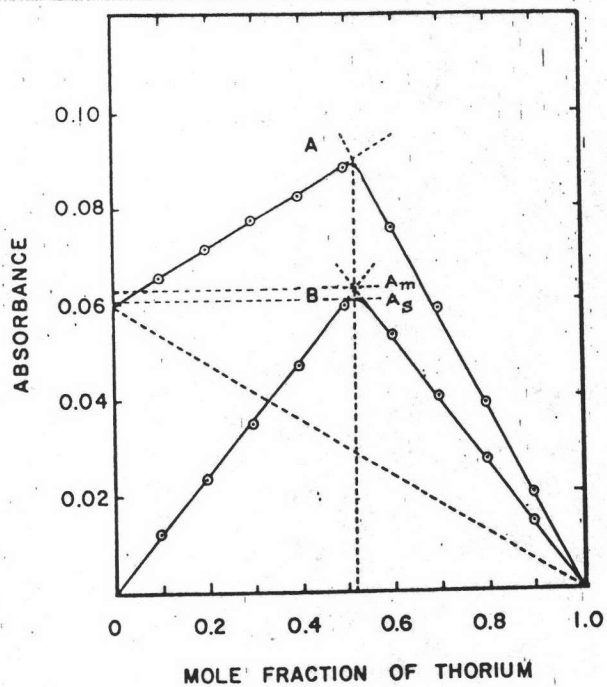


Fig.3.17: Continuous variation method

A = not corrected

B = corrected

Table 3.15 : The detailed data of the molar ratio method

| Th. 10^{-4} F (ml) | Absorbance at 610 nm | Th. 10^{-4} F (ml) | Absorbance at 610 nm |
|-------------------------|-------------------------|-------------------------|-------------------------|
| 0.0 | 0.000 | 4.0 | 0.109 |
| 0.2 | 0.004 | 4.5 | 0.118 |
| 0.5 | 0.010 | 5.0 | 0.129 |
| 1.0 | 0.022 | 6.0 | 0.139 |
| 1.5 | 0.036 | 7.0 | 0.141 |
| 2.0 | 0.052 | 8.0 | 0.146 |
| 2.5 | 0.068 | 9.0 | 0.146 |
| 3.0 | 0.084 | 10.0 | 0.146 |
| 3.5 | 0.098 | | |

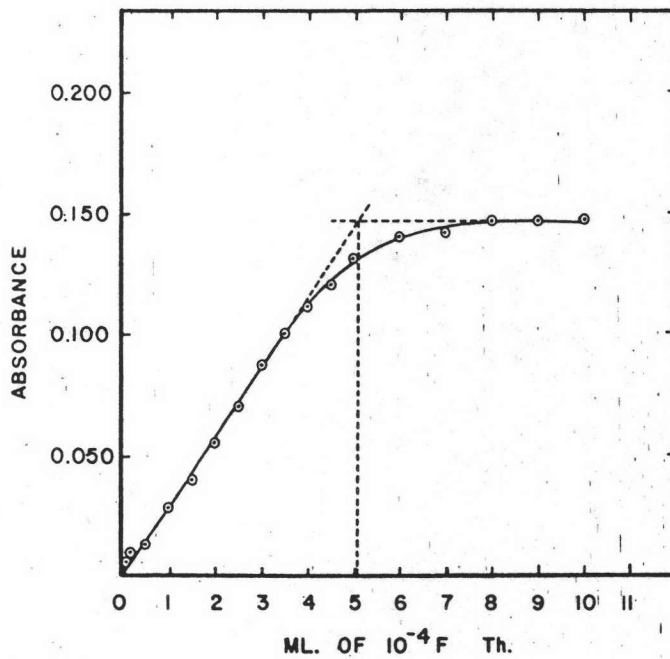


Fig. 3.18 : Mole ratio method

Fixed dye : 5 ml of 10^{-4} F.

Final volumn : 50 ml

the solutions were adjusted to 4.0 and final volumes were 50 ml. The absorbance of the solution was measured against a reagent at 610 nm using 1 cm cell. The detailed data is shown in Table 3.15 and the mole ratio plot is shown in Fig. 3.18.

From Fig. 3.18 ; the curve shows the deflection at a molar ratio of 1:1 metal:ligand complex.

3.5.5.3 Slope ratio Method

Procedure:

For the study by this method, two series of solution (series A and B) were prepared.

A. Condition of excess metal concentration

A series of solution were prepared by adding fixed amount of thorium solution (5 ml of 10^{-3} F solution) to the varied amount of dye solution (1-10 ml(S) of 10^{-4} F solution). The pH of each solution was adjusted to 4.0 by the addition of appropriate amount of 0.01 F nitric acid and then diluted to 50 ml with deionized water. The absorbance of solutions were measured at 610 nm against water as a reference using 1 cm cell. Data are shown in Table 3.16 with the corresponding plot in Fig. 3.19.

Table 3.16 : The detailed data on slope ratio method.

(A) thorium \gg m-x dye.(B) m-x dye \ll thorium

| (A) | | | (B) | | |
|-----------------------------|------------------------|----------------|-----------------------------|------------------------|----------------|
| m-x dye 10^{-4} F (ml) | Th 10^{-3} F (ml) | Abs. 610 nm | m-x dye 10^{-3} F (ml) | Th 10^{-4} F (ml) | Abs. 610 nm |
| 0 | 5 | 0.000 | 5 | 0 | 0.000 |
| 1 | 5 | 0.024 | 5 | 1 | 0.020 |
| 2 | 5 | 0.051 | 5 | 2 | 0.053 |
| 3 | 5 | 0.077 | 5 | 3 | 0.071 |
| 4 | 5 | 0.104 | 5 | 4 | 0.096 |
| 5 | 5 | 0.131 | 5 | 5 | 0.121 |
| 6 | 5 | 0.159 | 5 | 6 | 0.145 |
| 7 | 5 | 0.184 | 5 | 7 | 0.170 |
| 8 | 5 | 0.212 | 5 | 8 | 0.194 |
| 9 | 5 | 0.238 | 5 | 9 | 0.219 |
| 10 | 5 | 0.267 | 5 | 10 | 0.243 |

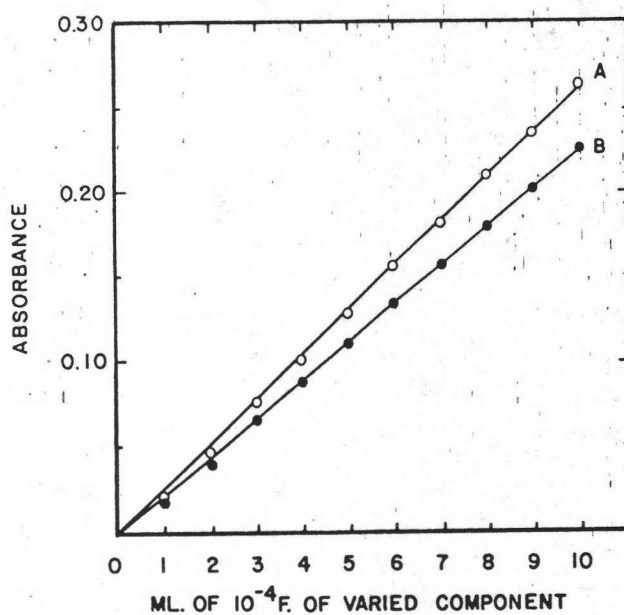


Fig 3.19 : Slope ratio method

A = Fixed Th. : 5 ml of 10^{-3} F.B = Fixed dye : 5 ml of 10^{-3} F.

Final volume : 50 ml

B. Condition of excess dye concentration

The procedure for the preparation of solutions were the same as described in A, except the fixed amount of 5 ml of 10^{-3} F dye solution and varied amount of thorium solution were employed. The absorbance of each solution was measured at 610 nm against reagent blank using 1 cm cell. Results are shown in Table 3.16 and Fig.3.19.

From the two curves, it is shown that the ratio of the slope of curve A to the slope of curve B is equal to 1:0.92 corresponding to 1:1 mole ratio of Th:dye complex.

Result obtained from the study of the nature of thorium-dye complex by method of continuous variation, mole ratio method and slope ratio method reveals that the 1:1 mole ratio of thorium:dye complex is formed. This is also confirmed by the absorption spectra of the complex in the next section.

Confirmation of the Nature of the Thorium - mX Dye Complex by Absorption Spectra

A series of solutions containing various molar ratio of dye to thorium were prepared. 5 ml of 10^{-4} F dye solution was used in each case with 2.5 ml, 5 ml, and 10 ml of 10^{-4} F thorium to make a mole ratio of dye to thorium of 2:1, 1:1, and 1:2 respectively. The pH of the solutions were adjusted to 4.0 by using 0.01 F HNO_3 .

The final volume is 50 ml. The spectra of the three solution systems were recorded from 550-700 nm using 1 cm cell and the reagent blank as reference. The results obtained are shown in Fig. 3.20.

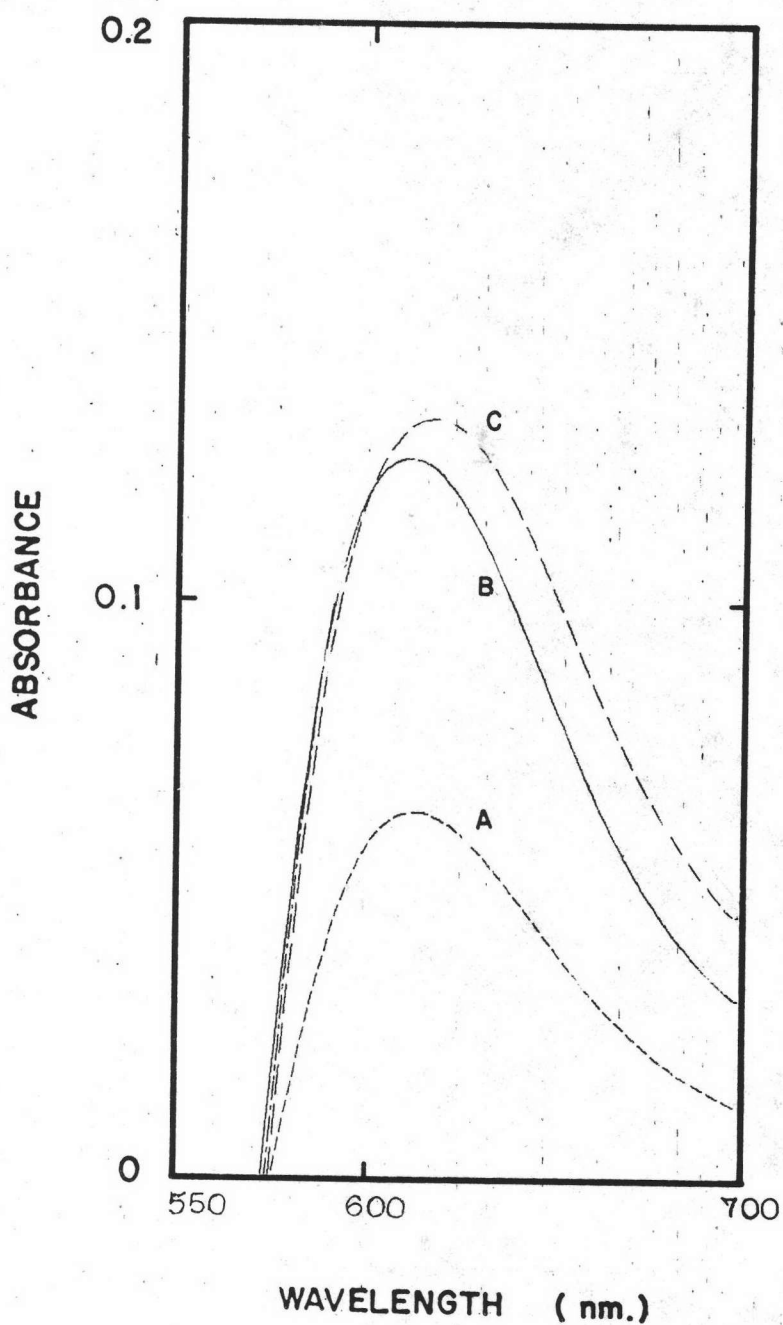


Fig. 3.20 : Absorption Spectra of various thorium - mX dye ratios at pH 4.0.

(A) 1 : 2 (B) 1 : 1 (C) 2 : 1

Reference : Reagent Blank

Final volume : 50 ml

3.6 Analytical Visible Spectrophotometric Studied of 1,4-bis(1,8-dihydroxy-3,6-disulfo-2-naphthylazo-benzene (p-X Dye).

Apparatus

The same set of instrument as previously described was used.

Reagents

Stock p-X Dye solution : A 10^{-3} F dye solution was prepared by dissolving 0.4214 g of the purified dyestuff in 500 ml of deionized water.

Standard thorium solution, 10^{-2} F. : The same stock solution as previously prepared was used.

pH adjustments : The same as preceding experiments.

3.6.1 Acid-Base Property of p-X Dye

Twelve 2 ml aliquots of 10^{-3} F p-X dye solution were used and the other steps is the same as m-X dye in the section 3.5.1. The experimental data is reported in Table 3.17.

The color changes resulted form Table 3.17 shows that p-X dye has acid-base property as same as m-X dye.

Table 3.17 : Colors observed at particular pH values of p-X dye

| pH | Color observed |
|----|----------------|
| 1 | orange |
| 2 | wine red |
| 3 | wine red |
| 4 | wine red |
| 5 | wine red |
| 6 | wine red |
| 7 | wine red |
| 8 | purple red |
| 9 | purple red |
| 10 | purple red |
| 11 | purple red |
| 12 | brownish red |

3.6.2 Visible Spectra of p-X Dye at Various pH values

Procedure :

The previously prepared obtained from 3.6.1 were used for the spectra study. The absorption spectra of p-X dye solutions at various pH values were recorded from the wavelength 400-650 nm using water as reference and 1 cm cell. The gain of the spectrophotometer was set at

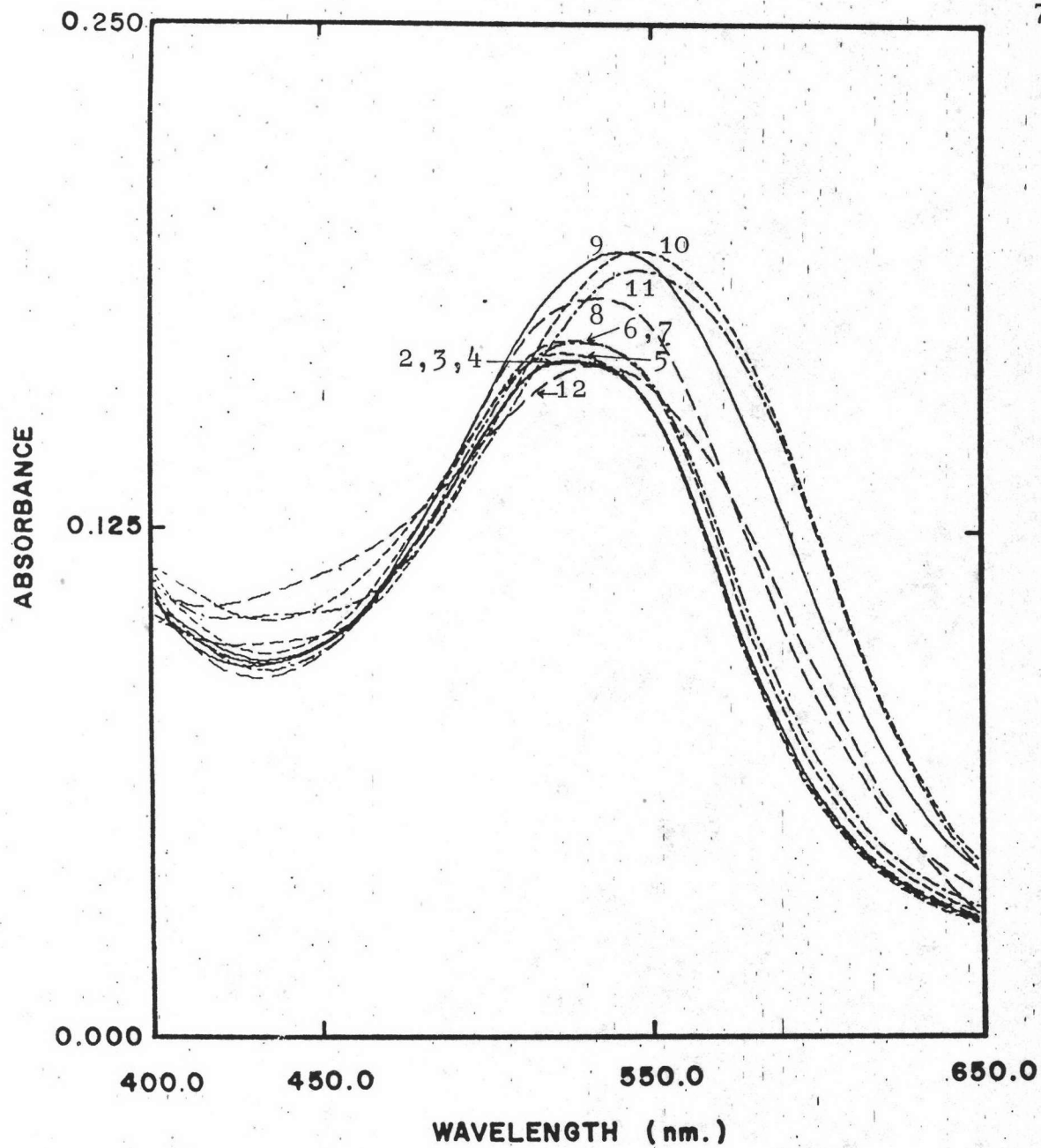


Fig.3.21 : Absorption Spectra of the Dye at various pH (2-12).

p-X Dye : 10^{-3} F , 2 ml

Final volume : 50 ml

Reference : Water

0-0.25, the slit width was 2.0 nm.

The absorption spectra obtained are shown in Fig. 3.21. The maximum absorbance occurs at about 530 nm over the pH range 2.0-7.0, and it shows a bathochromic shift above pH 8.0.

3.6.3 Visible Spectra of the Complex at Various pH.

Procedure

Seven 2 ml aliquots of 10^{-4} F thorium were pipetted into a series of 100 ml beaker containing accurately 2 ml each of 10^{-3} F p-X dye solution for studying thorium-pX dye complex. The pH of the solutions were adjusted to 2.0-6.0 using nitric acid or ammonia solution. The solutions were then transferred quantitatively into a series of 50 ml volumetric flasks. Small amount of water was added to the mark. The solutions were set aside for complete color development. The absorption spectra of the thorium-pX dye complex at pH 2.0-6.0 were recorded from 400-650 nm and 500-700 nm against water and reagent, respectively using 1 cm cell.

Figures 3.22 and 3.23 show the absorption spectra of the thorium-pX dye complex at various pH measured against water and reagent blank as references, respectively.

It was found that these solutions would be precipitate after the preparation for a half an hour. If the concentration of metal or reagent was reduced to

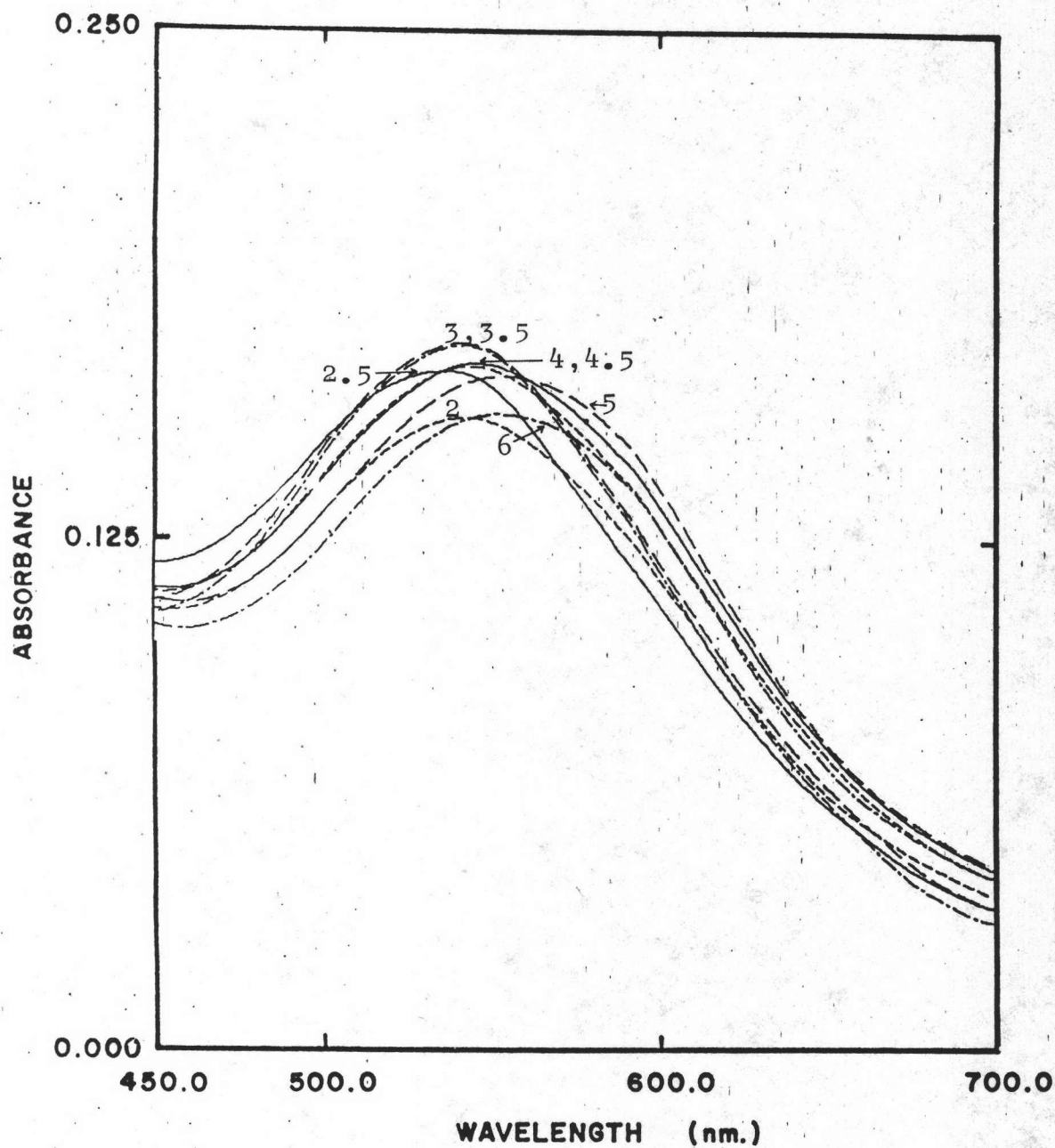


Fig.3.22 : Absorption spectra of thorium - dye complex at various pH (2.0 - 6.0).

Thorium : 10^{-4} F , 2 ml
 p-X Dye : 10^{-3} F , 2 ml
 Final volume : 50 ml
 Reference : Water

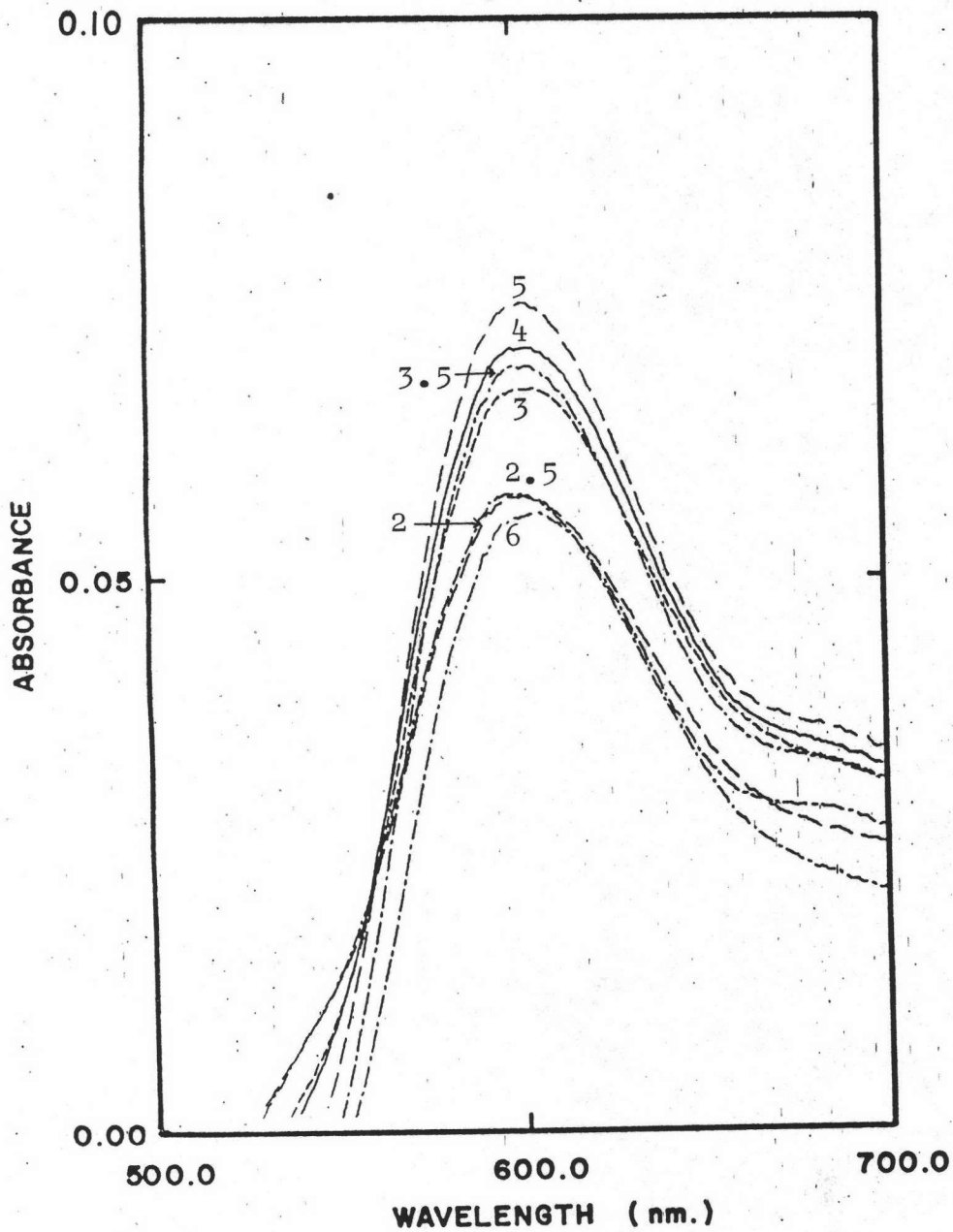


Fig. 3.23 : Absorption spectra of thorium - dye complex at various pH (2.0 - 6.0) .

| | | | |
|--------------|---|---------------|--------|
| Thorium | : | 10^{-4} F | , 2 ml |
| p-X Dye | : | 10^{-3} F | , 2 ml |
| Final volumn | : | 50 ml | |
| Reference | : | Reagent blank | |

avoiding the precipitation of the complex, the intensity of the color obtained would be decrease and difficult to observe or record the absorption spectra.

3.6.4 Spectrophotometric Determination of Thorium Using the p-X Dye as Metallochromic Reagents.

Optimal Conditions

Optimal Wavelength

The solution prepared in 3.6.3 was used for the investigation of the optimal analytical wavelength. The absorption spectra of the reagent and the complex at pH 4.0 were recorded from 450-700 nm. The free dye was measured against water as a reference. The complex was measured against both water and reagent blank. The absorption spectra of the reagent and the complex formed with thorium are shown in Fig 3.24. Inspection of the curves shows that at the wavelength of approximately 600 nm the greatest difference in absorbance between the blank and the complex is observed.

Optimal pH

The complex systems in the pH range from 2.0 to 7.0 were investigated. A series of solution containing 5 ml of 10^{-4} F thorium, 5 ml of 10^{-3} F p-X dye solution, and appropriate amount of water was prepared. The pH of solutions were adjusted by adding 0.1 F nitric acid or 0.1 F ammonia solution to 2.0-7.0. Each content was transferred

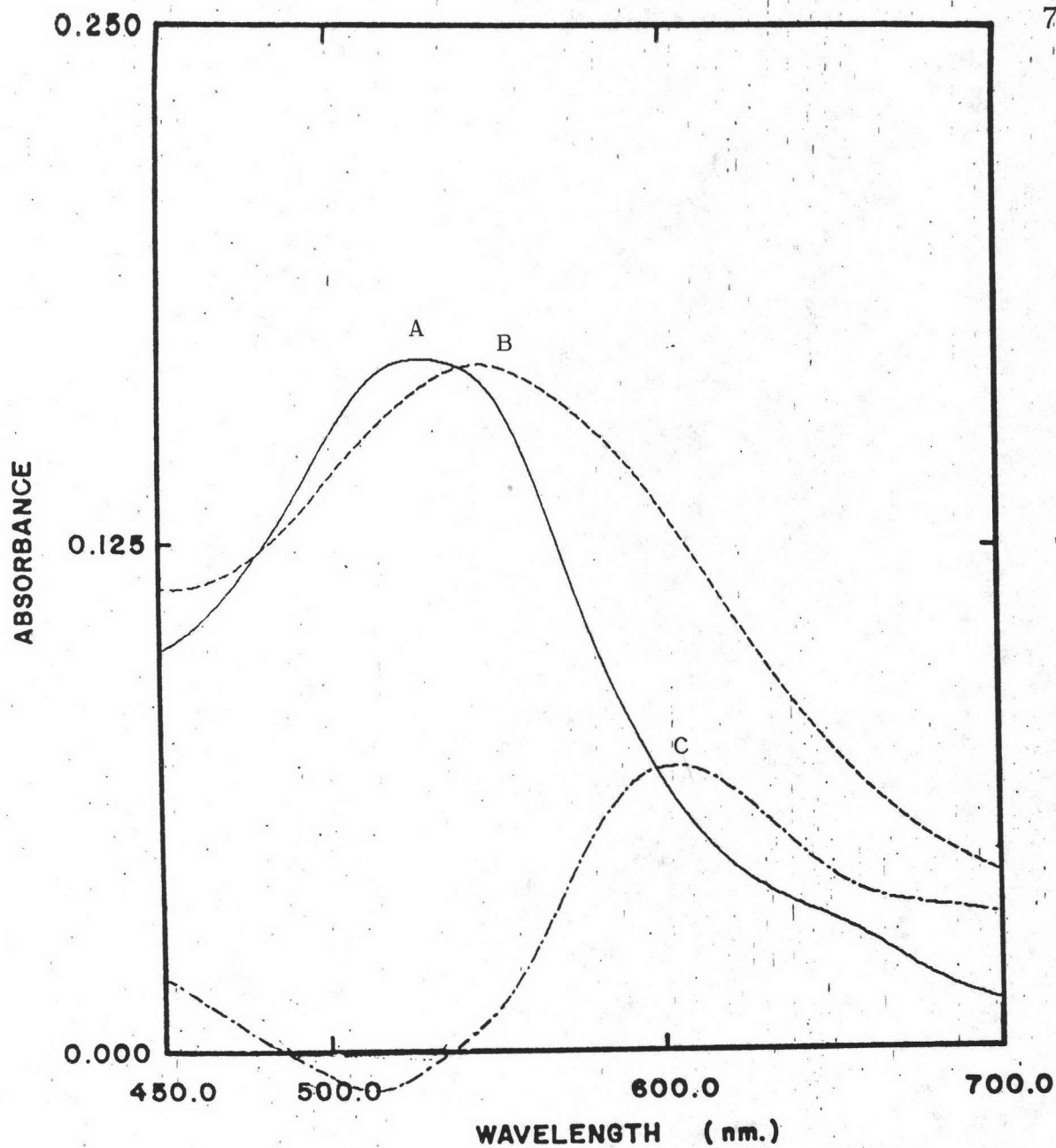


Fig.3.24 : Optimal wavelength of the dye and its thorium complex at pH 4.0.

A : p-X Dye 10^{-3} F , 2 ml

B : p-X Dye 10^{-3} F , 2 ml and Th. 10^{-3} F , 2 ml

C : A against B

Final volumn 50 ml

A and B were measured against water

Table 3.18: Optimal pH study of Th-pX Dye complex

| pH | Absorbance at 600 nm. |
|-----|-----------------------|
| 2.0 | 0.006 |
| 2.5 | 0.034 |
| 3.0 | 0.045 |
| 3.5 | 0.045 |
| 4.0 | 0.045 |
| 4.5 | 0.045 |
| 5.0 | 0.046 |
| 5.5 | 0.043 |
| 6.0 | 0.036 |
| 7.0 | 0.025 |
| 8.0 | 0.025 |

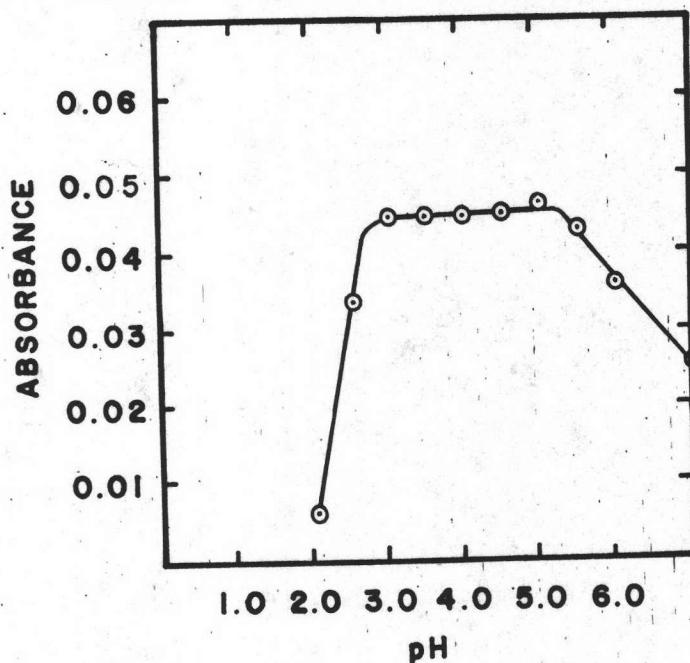


Fig. 3.25: Effect of pH on absorbance of thorium - pX dye complex measured against a reagent blank at 600 nm

p-X Dye : 5 ml of 10^{-3} F
 Thorium : 5 ml of 10^{-4} F
 Final volume : 50 ml

quantitatively to a 50 ml volumetric flask. The absorbance of each solution was measured against the corresponding reagent blank at 600 nm. The results are shown in Table 3.18 and the corresponding graph is in Fig. 3.25.

From Fig. 3.25, it is concluded that the optimal pH is in the range 3.0-5.0. Therefore, a pH of 4.0 was selected for all subsequent experiments.

Adherence to Beer-Bouguer-Lambert Law

Calibration Curve

Aliquots of 1 to 10 ml of 10^{-4} F thorium were pipetted into a series of 100 ml beakers containing pipetted 10 ml of 10^{-4} F p-x dye solution and appropriate amount of water. The pH of the solution was adjusted to 4.0 by using 0.01 F nitric acid and ammonia solution. The solution were then transferred quantitatively to a series of 50 ml volumetric flask. Small amount of deionized water was added to adjust the final volume. The absorbance of these solutions were measured at 600 nm against blank using 1 cm cell. The data obtained is shown in Table 3.19. The plot of the curve is shown in Fig. 3.26. It can be seen that the thorium complex obeys Beer-Bouguer-Lambert law over the concentration range from $4.6 \mu\text{g}$ up to about $58 \mu\text{g}$ of thorium in 50 ml.

Table 3.19: Calibration curve of thorium - pX dye complex

| p-X Dye 10^{-4} F (ml) | Th. 10^{-4} F | | Absorbance at 600 nm |
|-----------------------------|-----------------|----------|-------------------------|
| | (ml) | g/50 ml | |
| 10 | 0.2 | 4.6408 | 0.001 |
| 10 | 0.5 | 11.6019 | 0.004 |
| 10 | 0.8 | 18.5632 | 0.006 |
| 10 | 1.0 | 23.2038 | 0.008 |
| 10 | 1.5 | 34.8057 | 0.012 |
| 10 | 2.0 | 46.4076 | 0.016 |
| 10 | 2.5 | 58.0095 | 0.020 |
| 10 | 3.0 | 69.6114 | 0.021 |
| 10 | 4.0 | 92.8152 | 0.021 |
| 10 | 5.0 | 116.0190 | 0.021 |
| 10 | 6.0 | 139.2228 | 0.021 |
| 10 | 7.0 | 162.4266 | 0.021 |
| 10 | 10.0 | 232.0381 | 0.023 |

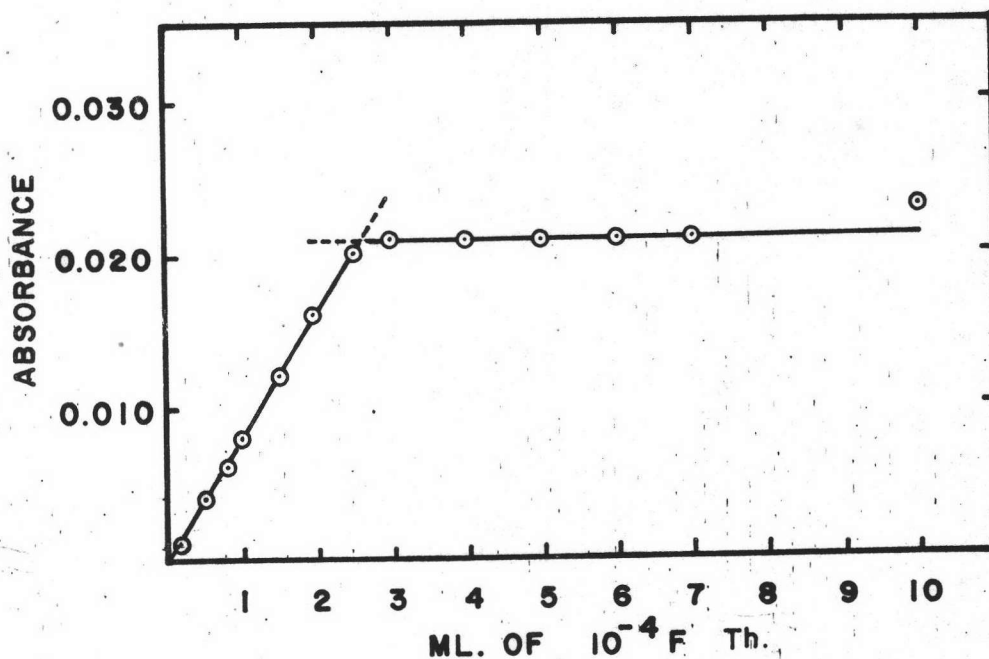


Fig.3.26: Calibration Curve of thorium - pX dye complex

Apparent absorptivity

With the standard thorium solution, the apparent absorptivity, a_m , is the slope of absorbance of the complex versus thorium concentration. It should be used in calculations only over the absorbance range that is linear. The absorptivities in the experiment were found to be 1×10^3 .

Taking this less sensitivity value and the preliminary investigation as shown in Table 3.3 into account, it may consequently not be of any practical values or worthwhile to carry out any further investigations of this p-X dye.