

CHAPTER 2

EXPERIMENTAL, RESULTS

AND DISCUSSION.



2.1 General Method for Preparation of Azo Compound.

Diazotization (27) is generally carried out in the following way. The amine is dissolved or suspended in an aqueous solution of mineral acid. More acid is used than the two equivalents per mole of amine that are required by the calculated value obtained from the chemical equation, the excess acid serves to keep the mixture strongly acidic which is necessary to prevent undesirable side-reaction. The mixture of amine and acid is cooled in an ice-salt mixture to the temperature between 0°C and -10°C . An aqueous solution of sodium nitrite is then added at such a rate that the temperature does not rise above $5-10^{\circ}\text{C}$ because the diazotization is an exothermic reaction. Although theoretically, the amount of sodium nitrite required for this reaction can be calculated. There is a loss of nitrous acid as nitric oxide and nitrogen dioxide. Consequently, it is essential to test the reaction mixture whether some more sodium nitrite should be added by means of starch-potassium iodide paper (28). The excess sodium nitrite which is not consumed by the amine will form nitrous acid. Nitrous acid as an oxidising agent converts iodide ion to a free iodine which reacts with starch giving a characteristic deep blue colour. The excess nitrous acid which interferes with subsequent reactions of the diazonium salt, can be destroyed by the addition of small amount of urea. Urea will react with nitrous acid giving off nitrogen, carbon dioxide and water.

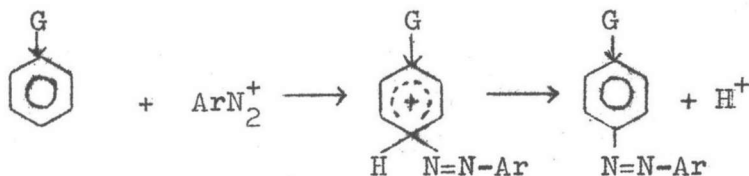
Since diazonium salts slowly decomposed even at ice-bath temperatures, the solution is used immediately after preparation.

Under the proper conditions, diazonium salts react with certain aromatic compound giving products of the general formula $\text{Ar-N}=\text{N-Ar}'$, called azo compounds. In this reaction, known as coupling, the nitrogen of the diazonium group is retained in the product, in contrast to the replacement reactions which nitrogen is lost; $(\text{ArN}_2^+ + \text{Z:} \longrightarrow \text{ArZ} + \text{N}_2)$



The aromatic ring ($\text{Ar}'\text{H}$) which attacked by the diazonium ion must, in general, contains powerful electron-releasing group, generally $-\text{OH}$, $-\text{NR}_2$, $-\text{NHR}$ or $-\text{NH}_2$ substitution usually occurs para to the activating group. Typically, coupling with phenol is carried out in mildly alkaline solution, and with amines in mildly acidic solution.

Activation by electron-releasing groups, as well as the evidence of kinetics studies, indicates that coupling is electrophilic aromatic substitution in which the diazonium ion is the attacking

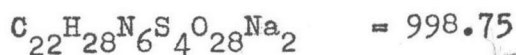
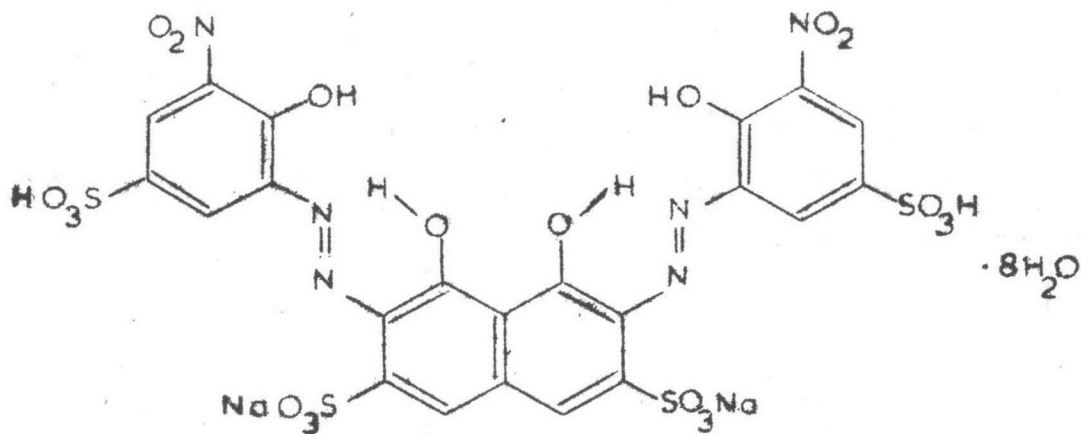


reagent:

It is significant that the aromatic compounds which undergo coupling are also the ones which undergo nitrosation. Like the nitrosonium ion, $+NO$, the diazonium ion, ArN_2^+ , is evidently very weakly electrophilic, and is capable of attacking only very reactive rings.

2.2 Preparation of 1,8-Dihydroxy-2,7-bis (2-hydroxy-3-nitro-5-sulpho-1-phenylazo)-naphthalene-3,6-disulphonic acid.

The proposed structural formula of the dye is as follows :(29)





2.2.1 Preparation of the dye.

Reagents.

- (1) Chromotropic acid, disodium salt (BDH).
- (2) 2-amino-6-nitrophenol-4-sulphonic acid, (MW \approx 234, about 75 % pure, Claytom Aniline Co. Ltd, Manchester)
- (3) Calcium chloride (Analar $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$)
- (4) Sodium nitrite.
- (5) Hydrochloric acid (Analar).
- (6) Sodium hydroxide (Analar).

Procedure (29)

To 250 ml of water was added 12.5 g. of 2-amino-6-nitrophenol-4-sulphonic acid which was suspended in 12 ml. of concentrated hydrochloric acid. After cooling in a freezing mixture (ice + NaCl) to 0°C , the content was diazotised by adding dropwise, with constant stirring, a cold solution of 2.8 g. of sodium nitrite in 20 ml. of water. A clear yellow solution of the diazonium salt was obtained in about 15 minutes.

A solution containing 3.6 g. of chromotropic acid (disodium salt) in 30 ml. of water was mixed with a solution of calcium chloride prepared by dissolving 7.0 g. of calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in 25 ml. of water, the whole was added to 50 ml. of 10 F. sodium hydroxide and cooled to 0°C . Into this solution was added dropwise, with constant stirring, the previously prepared diazonium salt solution. The temperature was kept below 5°C . After completing the addition, stirring was

continued for about 30 minutes the solution was then added to 70 ml. of concentrated hydrochloric acid and stored in a refrigerator overnight. After filtering through a sintered glass funnel, the precipitate was rinsed with 20 ml. of 6 F. hydrochloric acid and dried at 60°C for 24 hours.

2.2.2 Isolation and purification.

The dried dye, obtained from previous method was slowly dissolved with 25 ml. of water on a warm water bath. Then 25 ml. of concentrated hydrochloric acid was added and stored in the refrigerator. Filter through a sintered glass (No. 1) as previously described (see the preparation section) for three times.

2.2.3 Chromatographic studies of the dye

Paper chromatography (Ascending method)(30)

The compositions of mixed solvents.

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 results are shown in Table II.

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Table II

Various Mixed Solvent Systems with the Corresponding Rf Values

| system | solvent | ratio | Rf of sample | Rf of impurity |
|--------|--|--------|--------------|----------------|
| 1 | HCl : H ₂ O | 1:9 | 0.12 | 0.34 |
| 2 | HCl : H ₂ O | 1:19 | 0.16 | 0.4 |
| 3 | EtOH : HCl : H ₂ O | 1:1:10 | 0.17 | 0.42 |
| 4 | BuOH : NH ₄ OH : H ₂ O | 1:1:10 | 0.87 | 0.87 |
| 5 | EtOH : NH ₄ OH : H ₂ O | 1:1:10 | 0.93 | 0.93 |
| 6 | MeOH : HCl : H ₂ O | 1:1:10 | 0.13 | 0.39 |
| 7 | MeOH : NH ₄ OH : H ₂ O | 1:1:10 | 0.9 | 0.9 |
| 8 | HOAc : HCl : H ₂ O | 3:3:20 | 0.28 | 0.6 |
| 9 | BuOH : HCl : H ₂ O | 1:1:10 | 0.22 | 0.49 |

The solvent of system No.8 appeared to be the most suitable.

Procedure.

A few milligrams of the dye was dissolved in 2-3 drop of a mixed solvent (HOAc:HCl:H₂O = 3:3:20). A small amount of the solution was spotted on a 15x15 cm. filter paper (Whatman filter paper No.1) at the marked position (3 cm. from an edge), dried, and then rolled the paper as a cylindrical shape. The paper was immersed into an enclosed container which was contained about 2 cm. height of the same mixed solvent. The marked side of the paper was on the bottom of the container, so the marked position and the spot were about 1 cm. above the solvent. The system was set aside for 30 minutes and then removed the paper from the container. The position of the solvent front was marked immediately and the paper was allowed to dry in air.

After the third recrystallization, the dye sample showed by paper chromatography method to be reasonably pure (see Fig. I). The chromatogram shows that after the third recrystallization, the dye has only one component which indicates the high purity of the dye.

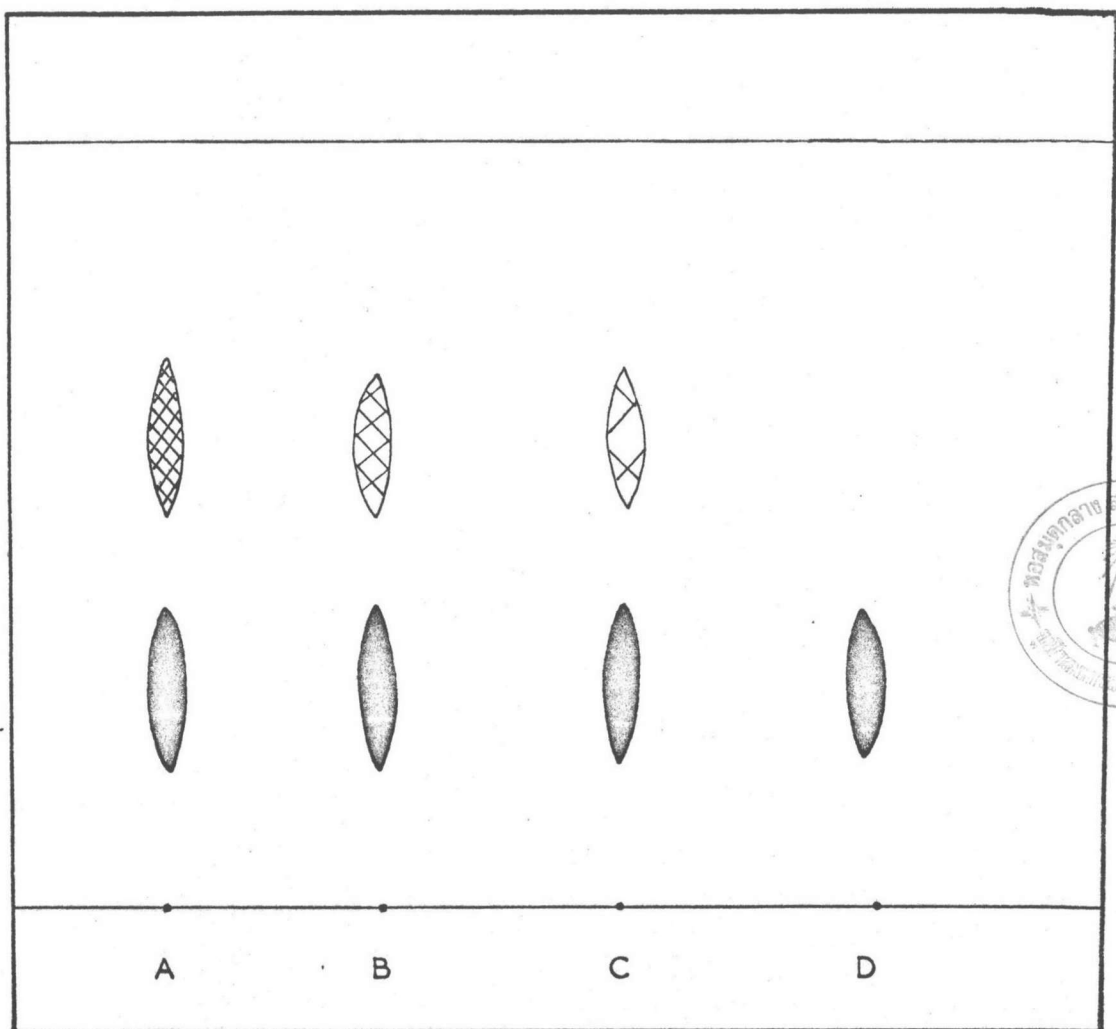


FIG. 1 Paper chromatographic study of the dye at various stages of crystallization.

- A : Crude dye
- B : 1st recrystallization
- C : 2nd recrystallization
- D : 3rd recrystallization

2.3 Systematic Study of the Dye as a Metallochromic

Reagent for Scandium.

2.3.1 Acid-base indicator property of the dye.

Procedure

A series of 10 ml. of 10^{-4} F. dye solution were pipetted to six 50-ml beakers. The pH of the content in each beaker was adjusted to the pH value of 1, 3.5, 4, 7, 11 and 12 by the addition of 0.1 F. and 1.0 F. hydrochloric acid or 0.1 F. and 1.0 F. sodium hydroxide. The pH value was recorded by a pH meter. The colour change of the dye solution was noted as shown in Table. III.

Table III

| pH | colour |
|-----|---------------|
| 1 | wine red |
| 3.5 | mauve blue |
| 4 | greenish blue |
| 7 | indigo |
| 11 | indigo |
| 12 | indigo |

From Table III, it indicates that this dye has an acid-base property.

2.3.2 Visible spectra of the dye at various pH values.

A. Instruments used.

1. Spectrophotometer.

A Perkin Elmer double-beam spectrophotometer model 124, with a Perkin Elmer 56 recorder, and 1 cm. silica cell were used for measuring the absorbance.

2. pH meter

A Radiometer pH meter type pH M28C manufactured by Messr. Electronic Measuring. Instruments, Copenhagen.

These instruments were used for measurements in all subsequent experiments throughout the course of this research work.

B. Reagents

10^{-2} F. stock solution of the dye. This was prepared by dissolving 0.9987 g. of the dye in 100 ml. of water and the solution was kept in the absence of the light in order to minimise the photochemical reaction of the dye.

C. Procedure

A series of 10 ml. of 10^{-4} F. dye solution were pipetted to fifteen 50-ml. beakers, followed by about 10 ml. of water. The contents in each beaker was adjusted to the pH value from 1 to 9 with the interval of 0.5 by adding an appropriate amount of either 0.1 F , 1.0 F. hydrochloric acid or 0.1 F. , 1.0 F sodium hydroxide.

The pH was recorded by the pH meter. Finally each content was transferred quantitatively to a 25-ml volumetric flask. The spectra were recorded against water from the wavelength 400-700 nm. The spectra are shown in Fig. 2

2.3.3 Visible spectra of dye-scandium complex.

Procedure.

Into two 50-ml. beakers, 10 ml. of 10^{-4} F. dye was pipetted. 1 ml. of 10^{-2} F.Sc(III) solution and about 10 ml. of water were added to one beaker. The other was added only 10 ml. of water. The pH of both was adjusted to the value of 2.5 by adding an appropriate amount of 0.1 F. hydrochloric acid and the pH was recorded by the pH meter. The contents were diluted to the final volume of 25 ml. The spectra of both were recorded against water from the wavelength 400-700 nm. as shown in Fig. 3.

2.4 Spectrophotometric Determination of Scandium Using the

Dye as a Reagent.

Experimental

A) Apparatus. The same set of instrument as previously described was used.

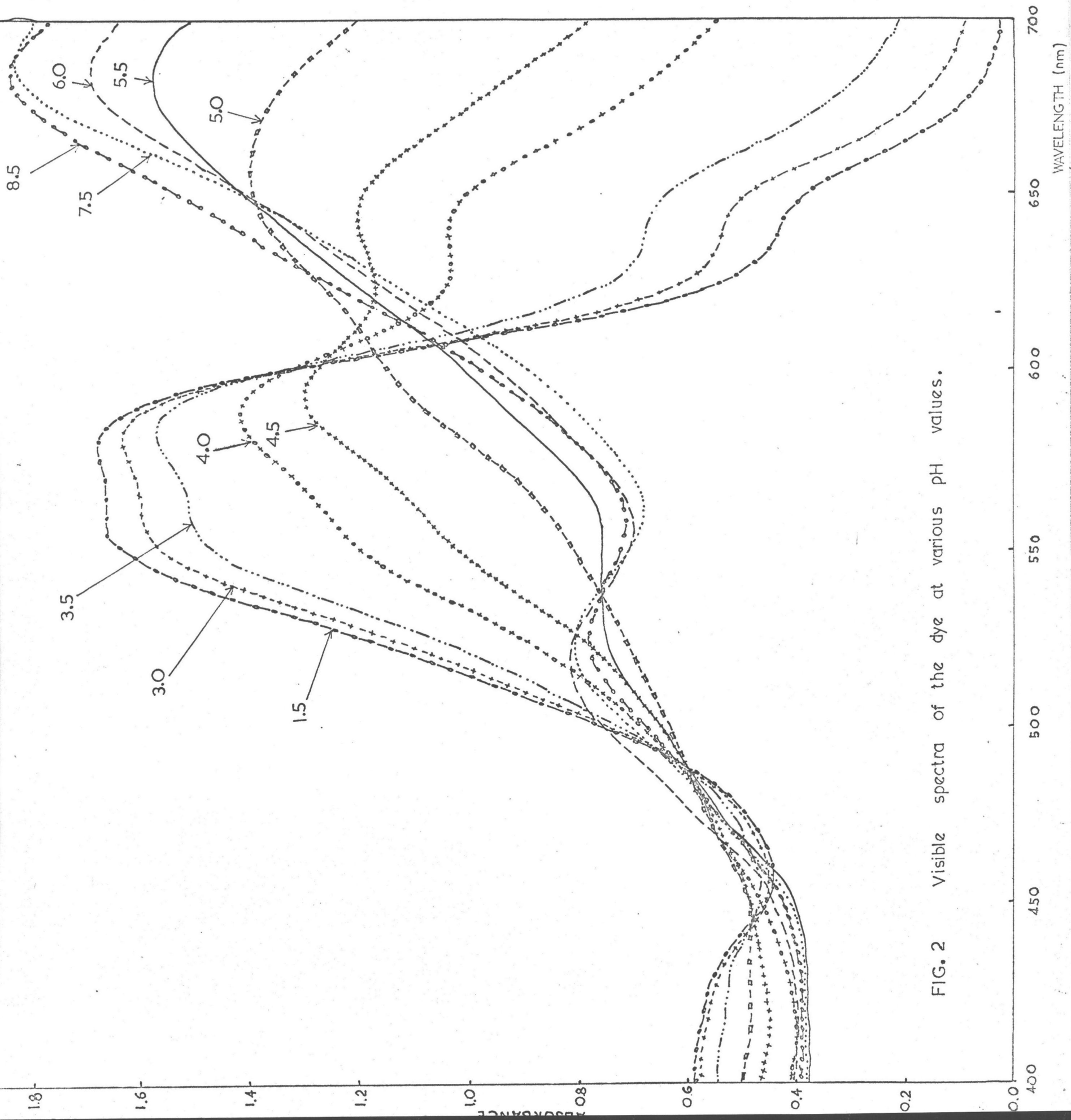


FIG. 2 Visible spectra of the dye at various pH values.

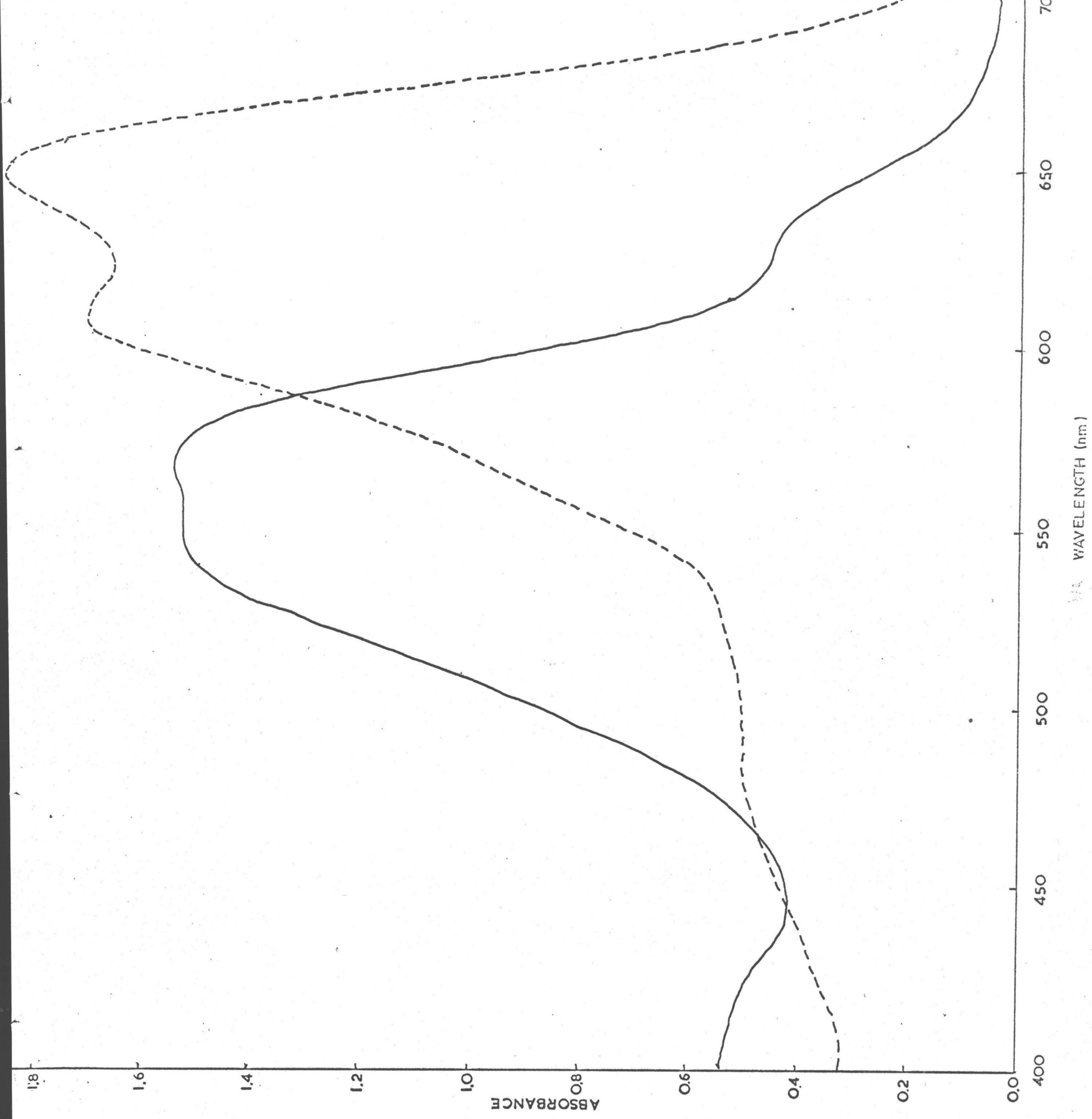


FIG. 3 Visible spectra of dye - scandium complex; - - - - - Sc-dye complex; — Dye.

B. Reagents.

Standard metal solution. Prepared by dissolving 0.06895 g. of B.D.H scandium oxide (99.9 %) with 5 ml. of concentrated hydrochloric acid. The solution was evaporated on a hot plate until the solution was clear and no more than 1 ml. of the solution was left, then diluted to 100 ml. with distilled water. The final concentration of the solution was 10^{-2} F. of scandium.

Stock solution of the dye. The same stock solution as previously prepared was used.

Diverse ion solutions. Solutions of diverse ions were prepared by dissolving known amounts of their pure compounds in distilled water. Dilute hydrochloric acid was used whenever necessary.

C. Procedure.

In order to determine scandium spectrophotometrically using this dye as a reagent, the following conditions should be carefully studied and established:

- 1.) Optimal wavelength for the scandium-dye complex.
- 2.) Optimal amount of the dye.
- 3.) Optimal pH.
- 4.) Optimal time for colour development.

2.4.1 Optimal wavelength.

10 ml. of 10^{-4} F. dye solution was pipetted into two 50-ml. beakers. One was followed by 2 ml. of 10^{-4} F. Sc (III) solution. The pH of both solutions was adjusted to the value of 2.5. Each content was transferred quantitatively to a 25 ml. volumetric flask. The spectra of the solutions were recorded using water as a reference, scanning from 400-700 nm. The spectra obtained are shown in Fig. 4

2.4.2 Optimal amount of the dye.

To six 50- ml.beakers, 4 ml. of 10^{-4} F. Sc (III) with varied volume of 10^{-4} F. dye as 4 ml, 8 ml, 10 ml, 12 ml, 14 ml, and 16 ml. and an appropriate amount of water were added. The pH of each solution was adjusted to 2.5 by the addition of 0.1F. hydrochloric acid. Each content was then transferred quantitatively to a 25 ml. volumetric flask. The absorbance of each solution was measured at 630 nm. against the reagent blank.

The absorbance of various ratio of dye to scandium at pH value of 2.5 are shown in Table IV and the corresponding plot appears in Fig. 5

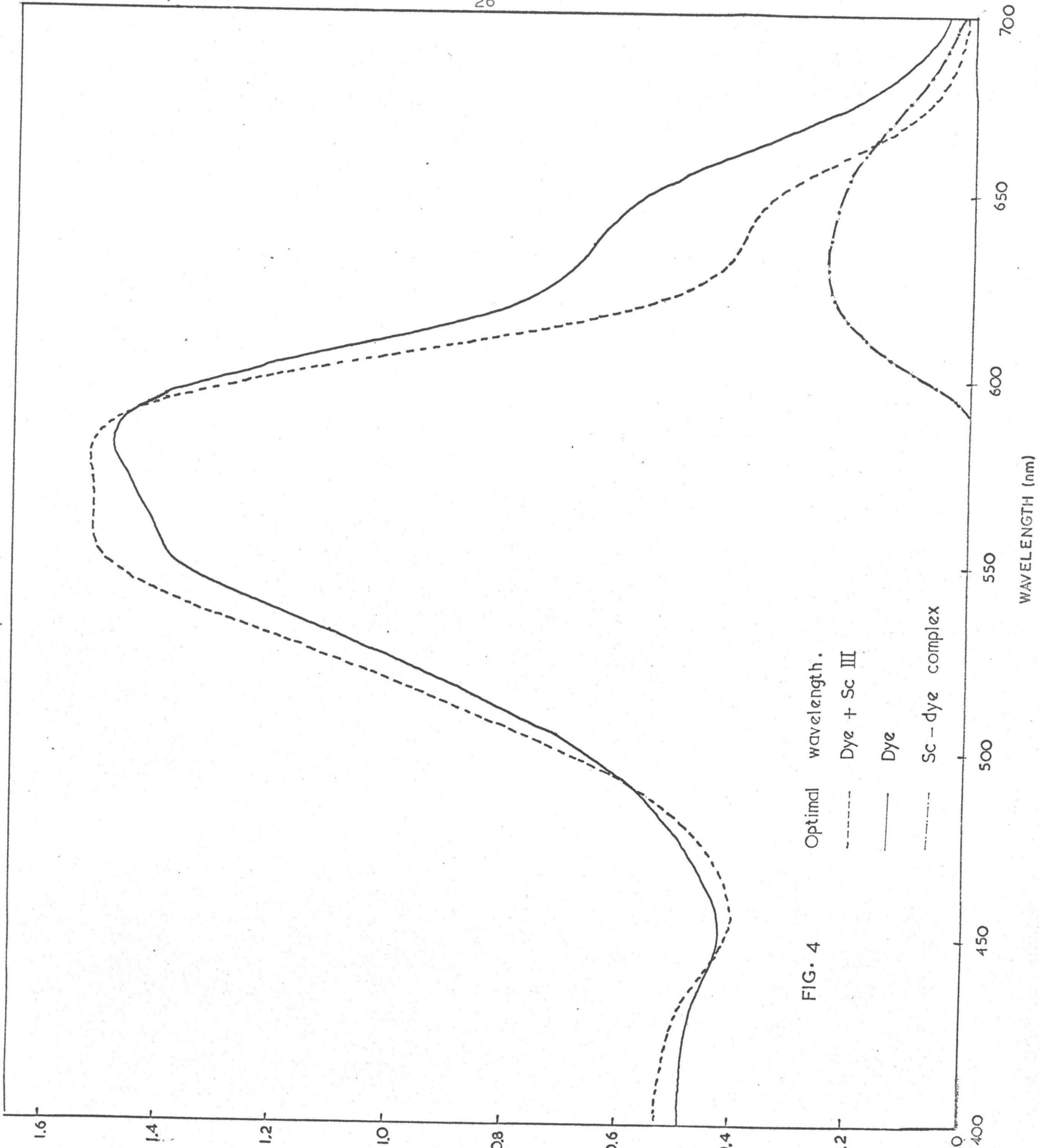


FIG. 4
Optimal wavelength.
Dye + Sc III
Dye
Sc-dye complex

WAVELENGTH (nm)

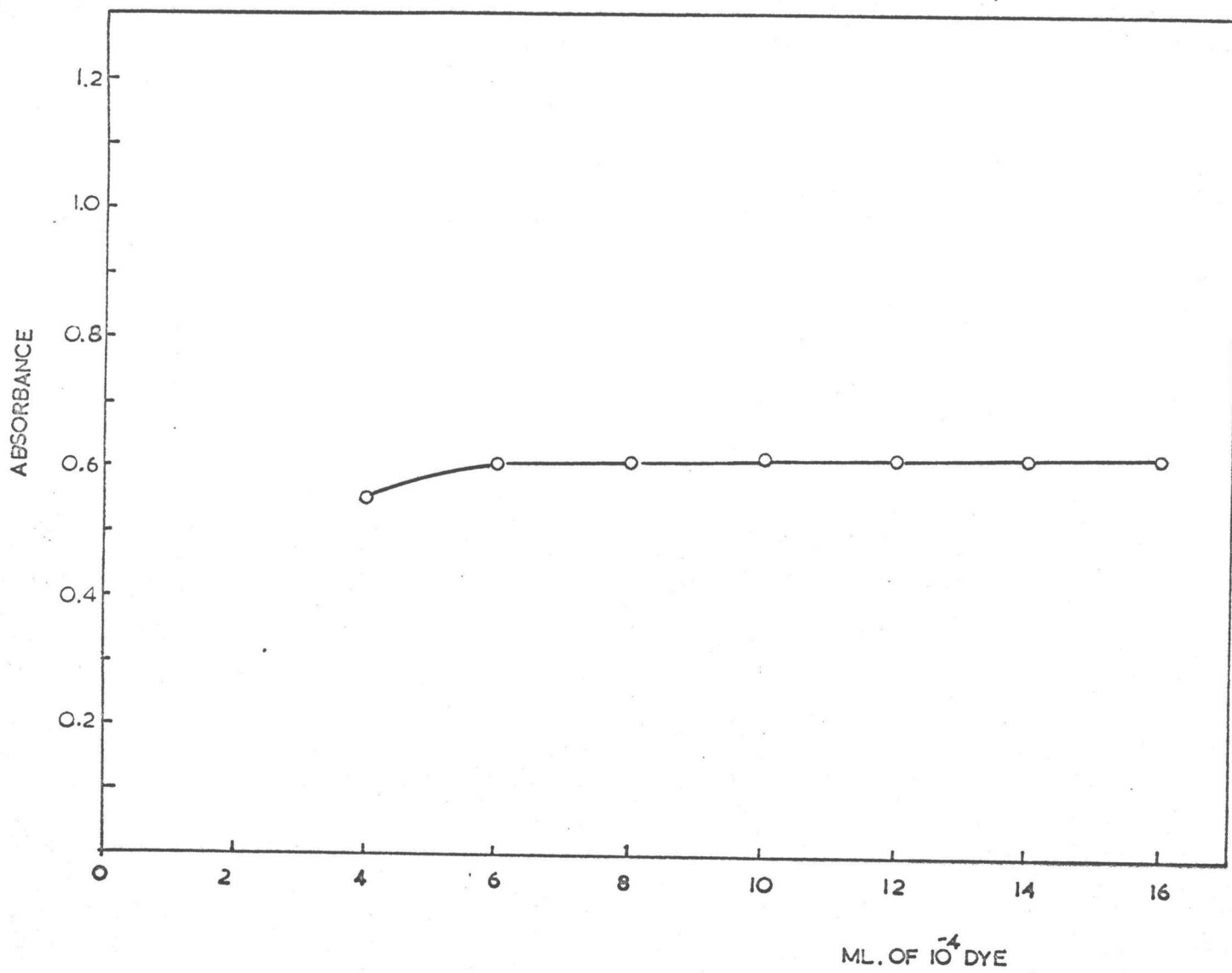


Fig. 5 Effect of the amount of the dye on the formation of the scandium-dye complex.

Table IV

| ml. of 10^{-4} F. dye | ml. of 10^{-4} F. Sc(III) | absorbance at 630 nm. |
|-------------------------|-----------------------------|-----------------------|
| 4 | 4 | 0.552 |
| 6 | 4 | 0.605 |
| 8 | 4 | 0.610 |
| 10 | 4 | 0.612 |
| 12 | 4 | 0.612 |
| 14 | 4 | 0.615 |
| 16 | 4 | 0.615 |

From Fig. 5, it can be seen that, the minimum amount of 10^{-4} F. dye required is 6 ml. In the subsequent experiments, 14 ml of 10^{-4} F. dye was selected and employed throughout the course of the work.

2.4.3 Optimal pH

To six 50-ml beakers, 2 ml. of 10^{-4} F. Sc(III), 14 ml. 10^{-4} F. dye and an appropriate amount of water were added. The pH of the solutions were adjusted by adding 0.1 F hydrochloric acid to pH 1, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0 respectively. Each content was transferred quantitatively to a 25-ml volumetric flask. The absorbance of each solution was measured against the corresponding reagent blank at 630 nm. The results are shown in Table V. and the corresponding graph is in Fig. 6 The spectra of the complex at various pH values are shown in Fig. 7

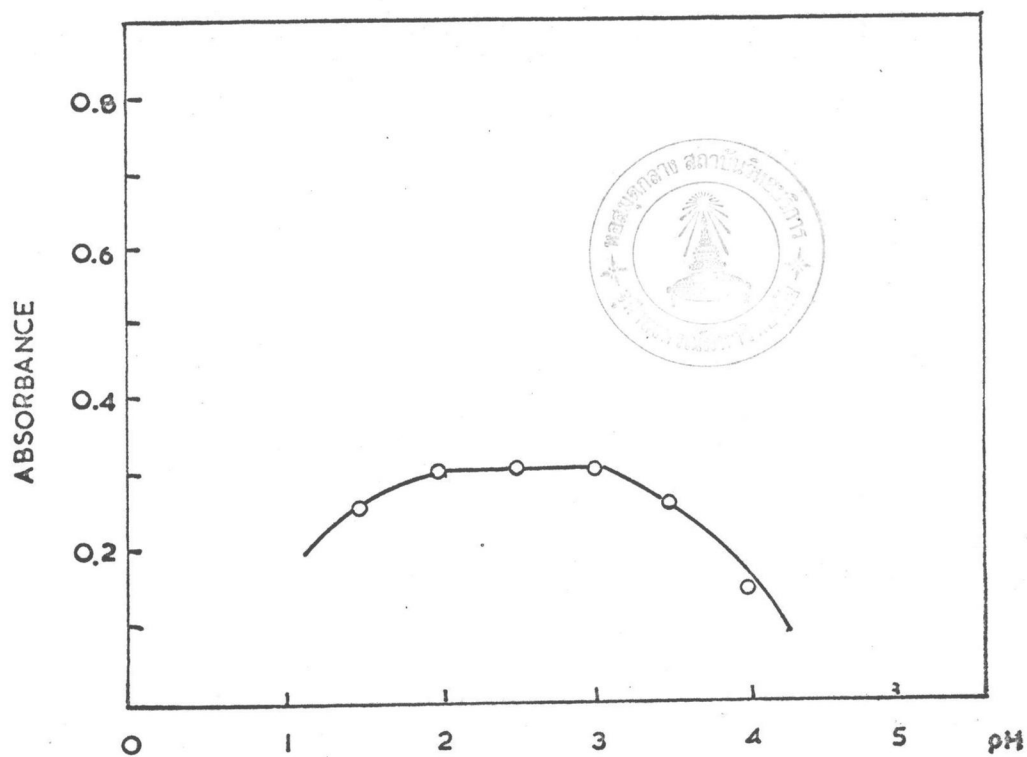


FIG. 6 Effect of pH on absorbance of scandium dye complex

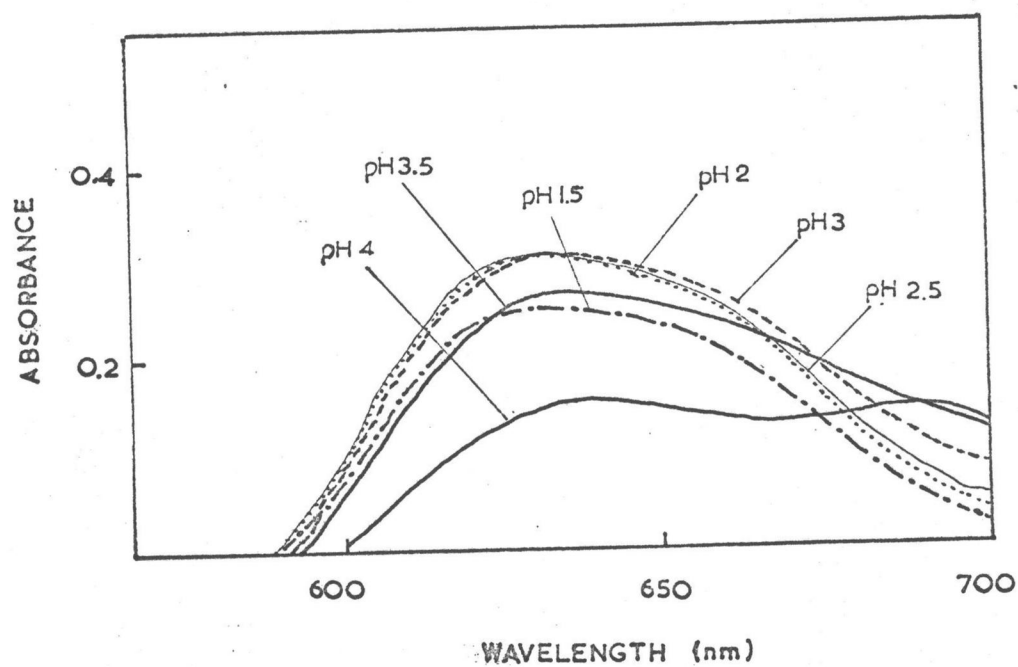


FIG. 7 The spectra of scandium dye complex at various pH value

Table V

| pH | absorbance at 630 nm. |
|-----|-----------------------|
| 1.5 | 0.250 |
| 2.0 | 0.303 |
| 2.5 | 0.303 |
| 3.0 | 0.303 |
| 3.5 | 0.262 |
| 4.0 | 0.145 |

From Fig.6, it is concluded that the optimal pH is in the range 2-3. In the subsequent experiments, pH 2.5 was selected.

2.4.4 Optimal time for colour development.

14 ml. of 10^{-4} F. dye was added to an appropriate amount of water in a 50-ml. beaker. The pH of the solution was adjusted to 2.5 by the addition of 0.1 F. hydrochloric acid. Then the solution was poured into a 25-ml. volumetric flask containing pipetted 2ml. 10^{-4} F. Sc(III) and adjusted to 25 ml. with distilled water if required. The absorbance was measured at 630 nm. against reagent blank at 0,5 min., 15 min., 30 min., etc. The result is shown in Table VI and the corresponding plot is in Fig. 8.

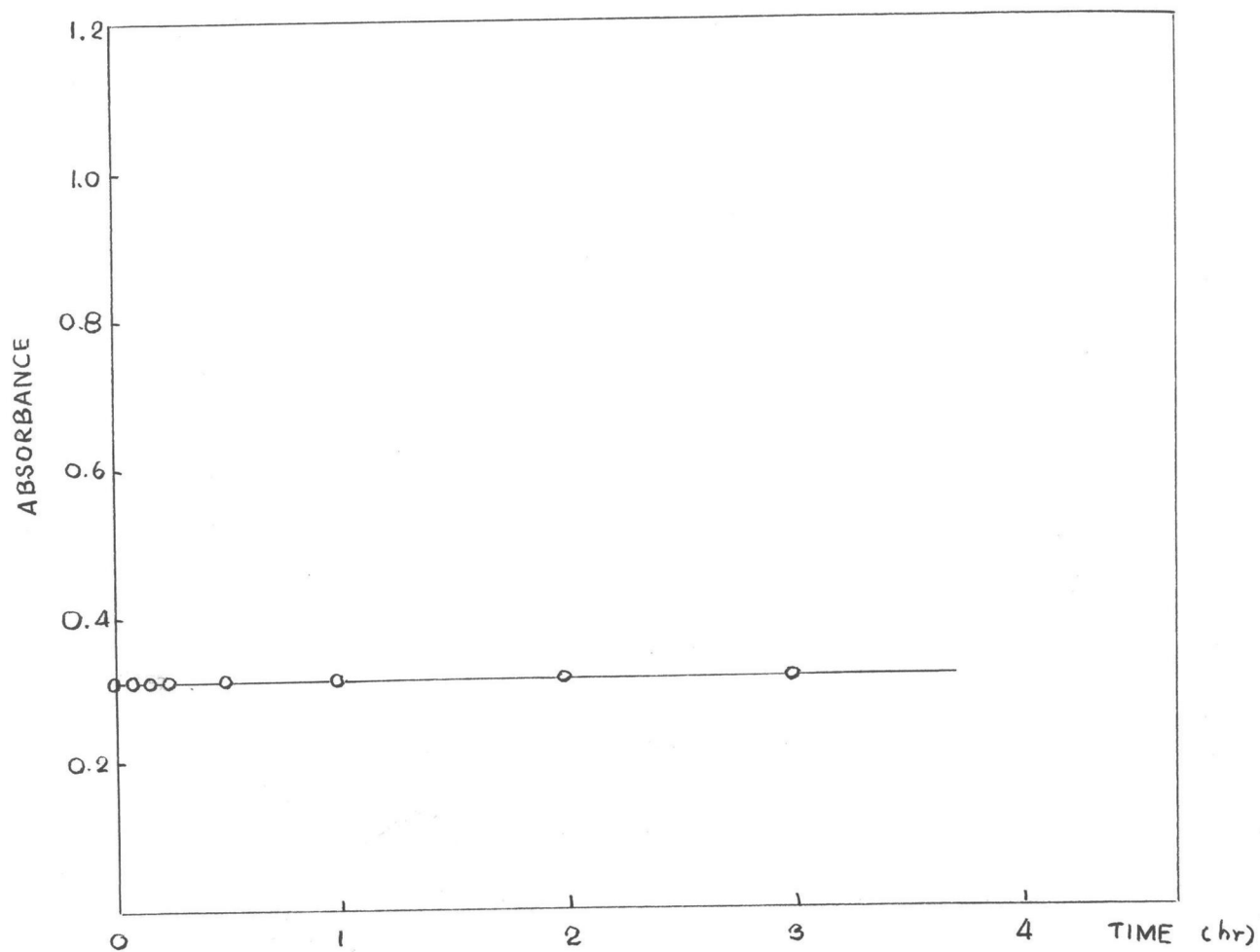


Fig. 8 The influence of time on the absorbance of the scandium-dye complex.

Table VI

| time | absorbance at 630 nm. |
|---------|-----------------------|
| 0 min. | 0.310 |
| 5 min. | 0.310 |
| 15 min. | 0.310 |
| 30 min. | 0.310 |
| 1 hr. | 0.310 |
| 2 hr. | 0.310 |
| 3 hr. | 0.315 |
| 6 hr. | 0.305 |
| 12 hr. | 0.300 |
| 24 hr. | 0.300 |

From Fig. 8, it can be seen that the colour of the complex is developed immediately and remains constant at least 24 hours.

2.4.5 Lambert-Beer law check

To a series of fifteen 50-ml. beakers were added 14 ml. of 10^{-4} F. dye solution, followed by a series of 0.18-2.70 ppm. of Sc(III) solution. The pH of the solutions were adjusted to 2.5 by the addition of 0.1 F. hydrochloric acid. The solution in each beaker was transferred quantitatively to a 25 ml. volumetric flask and diluted to the mark. The absorbance of these solutions were measured at 630 nm. against reagent blank as the reference.

The calibration curve is found to obey Lambert-Beer law very well over the range of 0.18 ppm. to 1.44 ppm. of scandium as shown in Table VII and Fig. 9

Table VII



| ml. of 10^{-4} F.dye | ml. of 10^{-4} F.Sc(III) = X ppm. | absorbance at 630 nm. |
|------------------------|-------------------------------------|-----------------------|
| 14 | 1 = 0.18 | 0.145 |
| 14 | 2 = 0.36 | 0.300 |
| 14 | 3 = 0.54 | 0.455 |
| 14 | 4 = 0.72 | 0.615 |
| 14 | 5 = 0.90 | 0.762 |
| 14 | 6 = 1.08 | 0.915 |
| 14 | 7 = 1.26 | 1.070 |
| 14 | 8 = 1.44 | 1.210 |
| 14 | 9 = 1.62 | 1.340 |
| 14 | 10 (1.0 ml of 10^{-3} F) = 1.80 | 1.400 |
| 14 | 11 (1.1 ml of 10^{-3} F) = 1.98 | 1.460 |
| 14 | 12 (1.2 ml of 10^{-3} F) = 2.10 | 1.530 |
| 14 | 13 (1.3 ml of 10^{-3} F) = 2.34 | 1.540 |
| 14 | 14 (1.4 ml of 10^{-3} F) = 2.52 | 1.560 |
| 14 | 15 (1.5 ml of 10^{-3} F) = 2.70 | 1.560 |

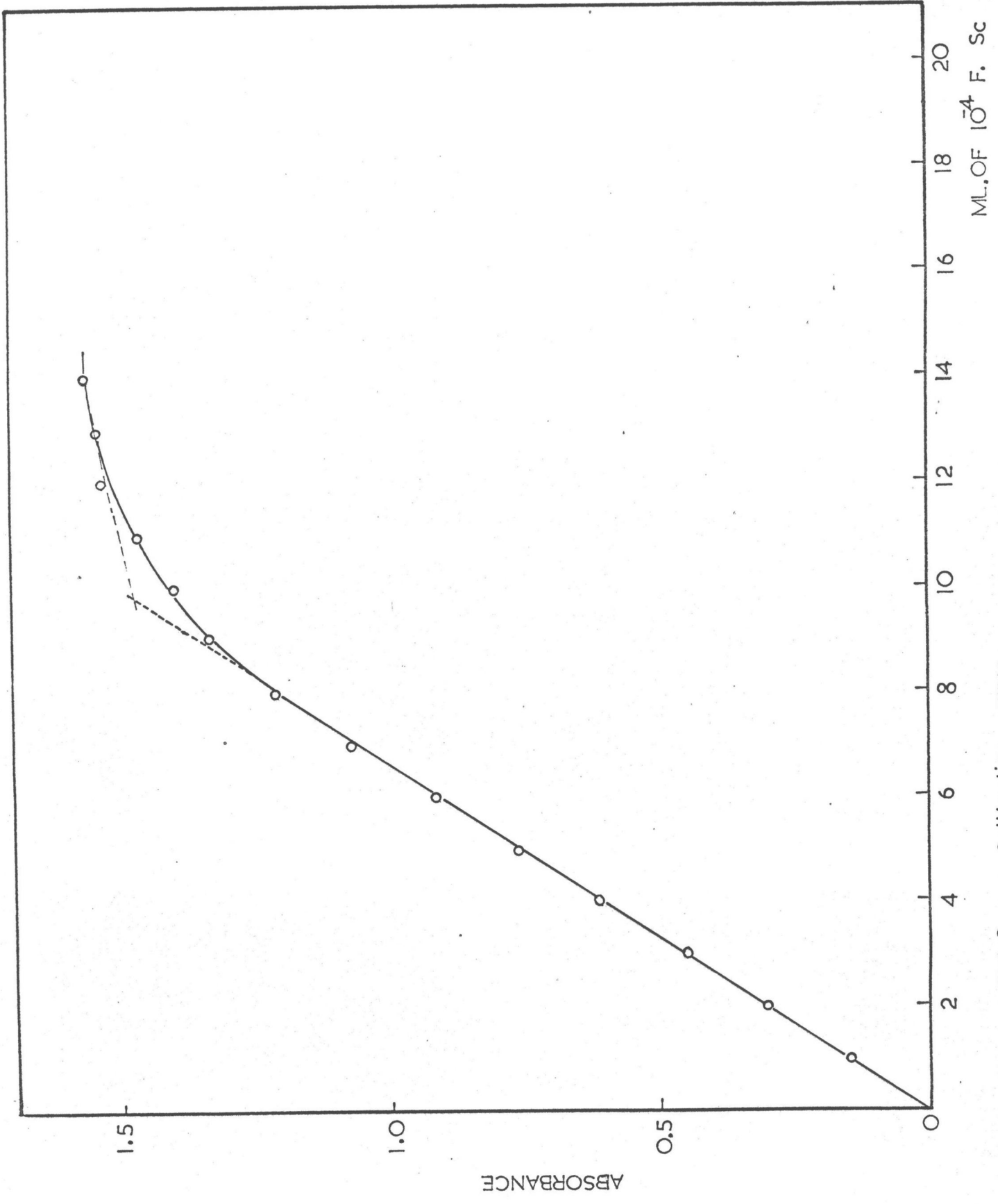


FIG.9 Calibration curve

2.4.6 Reproducibility of the method

The reproducibility of this method was checked by means of the standard deviation of the determination which obtained from measuring the absorbance of 10 set of solutions, each containing a final scandium concentration of 2 ml 10^{-4} F. in the total volume of 25 ml. and the pH was 2.5. The absorbance of each solution was measured at 630 nm. The results are shown in Table VIII

Table VIII

| ml. of 10^{-4} F. dye | ml. of 10^{-4} F. Sc(III) | absorbance at 630 nm. |
|-------------------------|-----------------------------|-----------------------|
| 14 | 2 | 0.310 |
| 14 | 2 | 0.300 |
| 14 | 2 | 0.310 |
| 14 | 2 | 0.302 |
| 14 | 2 | 0.300 |
| 14 | 2 | 0.310 |
| 14 | 2 | 0.315 |
| 14 | 2 | 0.300 |
| 14 | 2 | 0.303 |
| 14 | 2 | 0.305 |

Calculation

| absorbance at 630 nm. | $d = (\bar{x} - x)$ | d^2 |
|-----------------------|---------------------|----------|
| 0.310 | -0.005 | 0.000025 |
| 0.300 | +0.005 | 0.000025 |
| 0.310 | -0.005 | 0.000025 |
| 0.302 | +0.003 | 0.000009 |
| 0.300 | +0.005 | 0.000025 |
| 0.310 | -0.005 | 0.000025 |
| 0.315 | +0.010 | 0.000100 |
| 0.300 | +0.005 | 0.000025 |
| 0.303 | +0.002 | 0.000004 |
| 0.305 | 0.000 | 0.000000 |

$$\bar{x} = \text{average value} = 0.305$$

$$\begin{aligned} \text{standard deviation } \delta &= \pm \sqrt{\frac{\sum d^2}{N-1}} \\ &= \pm \sqrt{\frac{0.000188}{9}} \\ &= \pm \sqrt{0.0000209} \\ \delta &\approx \pm 0.0044 \end{aligned}$$

$$\text{The coefficient of variation} = 1.3 \%$$

2.4.7 Diverse ion study.

The effect of twenty cations and seven anions on the scandium determination were investigated. The limiting value of the concentration of a foreign ion was taken as that which caused an error of $\pm 5\%$ in the determination of 1 ml of $10^{-4}F$ scandium in the final volume of 25 ml. The results obtained are summarized in Table IX

Table IX

Influence of Diverse Ions on the Determination of Scandium

| Diverse ion | Molar ratio (X : Sc) | Absorbance at 630 nm. |
|------------------|-------------------------|--------------------------|
| Cu ⁺⁺ | 100 | >2 |
| | 10 | 1.490 |
| | 1 | 0.265 |
| | 0.5 | 0.208 |
| | 0.1 | 0.165 |
| | 0.04 | 0.148 |
| Ni ⁺⁺ | 100 | 0.81 |
| | 10 | 0.542 |
| | 1 | 0.19 |
| | 0.5 | 0.165 |
| | 0.04 | 0.155 |

Table IX (continued)

| Diverse ion | Molar ratio (X : Sc) | Absorbance at 630 nm. |
|-------------------|-------------------------|--------------------------|
| Co ⁺⁺ | 100 | 0.413 |
| | 10 | 0.184 |
| | 1 | 0.160 |
| | 0.5 | 0.155 |
| Mg ⁺⁺ | 100 | 0.173 |
| | 10 | 0.165 |
| | 1 | 0.145 |
| Pb ⁺⁺ | 100 | 0.213 |
| | 10 | 0.165 |
| | 1 | 0.150 |
| Al ⁺⁺⁺ | 100 | 1.730 |
| | 10 | 0.645 |
| | 1 | 0.190 |
| | 0.5 | 0.170 |
| | 0.1 | 0.155 |
| Mn ⁺⁺ | 100 | 0.190 |
| | 50 | 0.155 |
| | 10 | 0.150 |

Table IX (continued)

| Diverse ion | Molar ratio (X : Sc) | Absorbance at 630 nm. |
|-----------------------|-------------------------|--------------------------|
| Mo ⁺⁶ | 100 | 1.040 |
| | 10 | 1.010 |
| | 1 | 0.200 |
| | 0.50 | 0.195 |
| | 0.10 | 0.160 |
| | 0.04 | 0.142 |
| Hg ⁺⁺ | 100 | 1.620 |
| | 10 | 0.158 |
| | 1 | 0.145 |
| Sn ⁺⁺ | ppt. | |
| UO ⁺⁺ 2 | 100 | 1.440 |
| | 10 | 1.100 |
| | 1 | 0.270 |
| | 0.50 | 0.235 |
| | 0.10 | 0.160 |
| | 0.04 | 0.145 |
| Cr ⁺³ | 100 | 0.220 |
| | 10 | 0.200 |
| | 1 | 0.145 |

Table IX (continued)

| Diverse ion | Molar ratio (X : Sc) | Absorbance at 630 nm. |
|--------------------|--------------------------|--------------------------|
| Ba ⁺⁺ | 100 | 0.183 |
| | 50 | 0.175 |
| | 10 | 0.155 |
| Sr ⁺⁺ | 100 | 0.180 |
| | 50 | 0.165 |
| | 10 | 0.145 |
| Th ⁺⁺⁺⁺ | 100 | 1.850 |
| | 10 | 1.130 |
| | 1 | 0.560 |
| | 0.5 | 0.393 |
| | 0.1 | 0.202 |
| | 0.04 | 0.145 |
| | 0.01 | 0.145 |
| Ca ⁺⁺ | 100 | 0.145 |
| Cd ⁺⁺ | 100 | 0.145 |
| Fe ⁺⁺ | 100 | 0.342 |
| | 10 | 0.255 |
| | 1 | 0.210 |
| | 0.5 | 0.198 |
| | 0.1 | 0.165 |
| | 0.04 | 0.145 |

Table IX (continued)

| Diverse ion | Molar ratio (X : Sc) | Absorbance at 630 nm |
|------------------------------|-------------------------|-------------------------|
| La ⁺⁺⁺ | 100 | 0 |
| | 50 | 0.19 |
| | 10 | 0.215 |
| | 1 | 0.18 |
| | 0.5 | 0.152 |
| | 0.04 | 0.15 |
| Na ⁺ | 100 | 0.155 |
| citrate | 100 | 0.158 |
| SO ₄ ⁼ | 100 | 0.155 |
| NO ₃ ⁻ | 100 | 0.158 |
| Cl ⁻ | 100 | 0.152 |
| acetate | 100 | 0.15 |
| PO ₄ ⁼ | 100 | 0.145 |
| F ⁻ | 100 | 0.04 |
| | 10 | 0.15 |

The absorbance of Sc-dye complex = 0.15

2.4.8 Recommended method for spectrophotometric determination of scandium.

Place a solution containing 0.18 ppm to 1.44 ppm of scandium in a 50 ml. beaker and add 14 ml. of 10^{-4} F. dye solution. Adjust the pH to 2.5 by adding an appropriate amount of 0.01 F. hydrochloric acid. The solution is transferred quantitatively to a 25 ml volumetric flask and dilute to the mark with water. Measure the absorbance of the solution at 630 nm against the corresponding reagent blank.

2.5 Stoichiometry of Scandium-Dye Complex

2.5.1 Method of continuous variation (31)

10^{-4} F. solutions of scandium ion and dye were mixed in complementary preparations to a total volume of 10 ml. After adjustment of acidity to pH 2.5, the mixtures were diluted to 25 ml. and measured the absorbance against water as the reference at 630 nm. Results are shown in Table X and the plot of absorbance against mole fraction is shown in Fig. 10

Table X

| ml.of 10^{-4} F.dye | ml.of 10^{-4} F.Sc(III) | mole fraction of scandium | Absorbance at 630 nm. |
|--------------------------|------------------------------|------------------------------|--------------------------|
| 0 | 10 | 1.0 | 0.000 |
| 1 | 9 | 0.9 | 0.195 |
| 2 | 8 | 0.8 | 0.385 |
| 3 | 7 | 0.7 | 0.575 |
| 4 | 6 | 0.6 | 0.755 |
| 5 | 5 | 0.5 | 0.953 |
| 6 | 4 | 0.4 | 0.945 |
| 7 | 3 | 0.3 | 0.822 |
| 8 | 2 | 0.2 | 0.715 |
| 9 | 1 | 0.1 | 0.632 |
| 10 | 0 | 0.0 | 0.505 |

From Fig.10, it is evident that the formation of 1:1 scandium-dye complex is indicated.

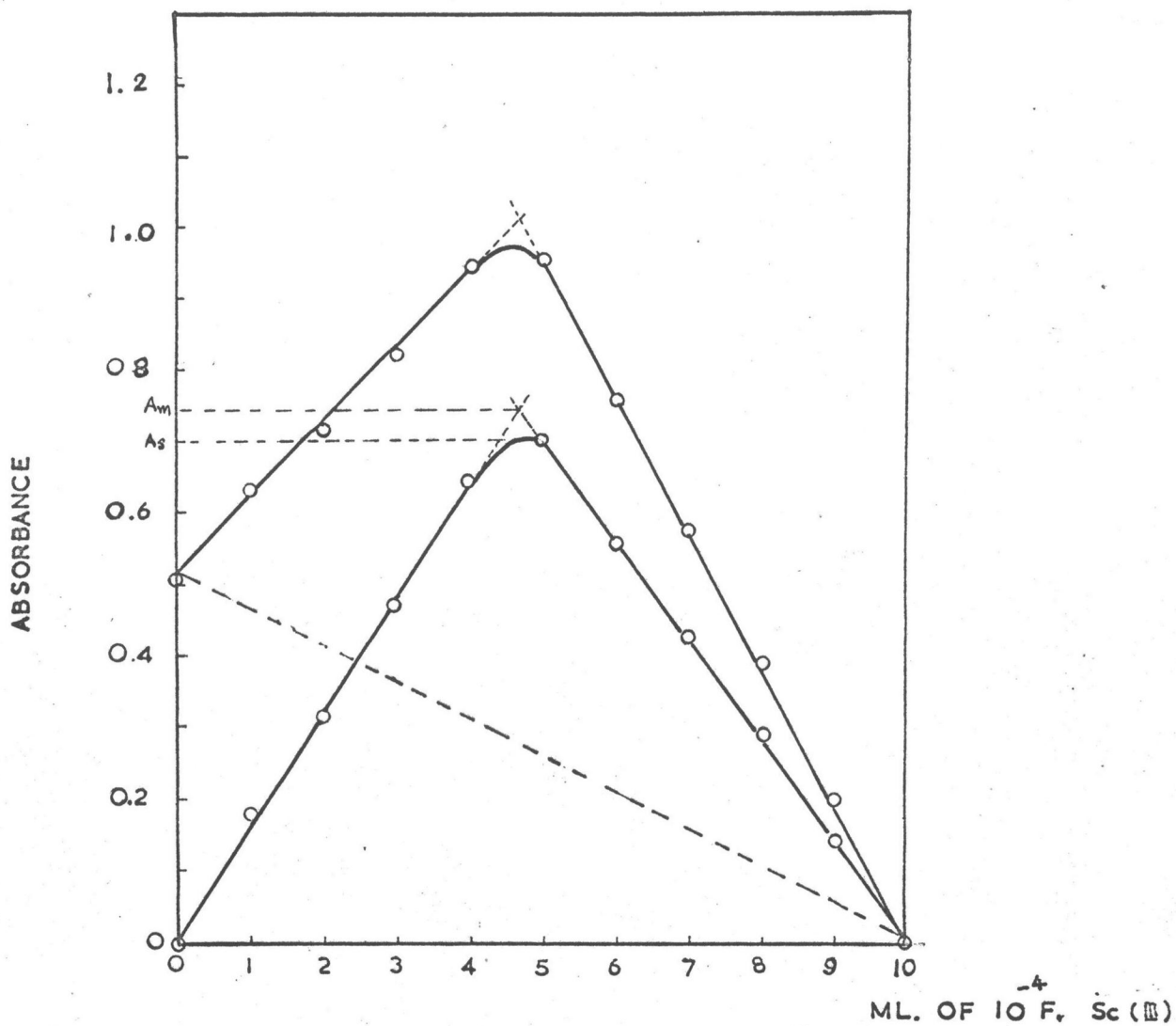


Fig. 10 Job's method of continuous variation



2.5.2 Mole ratio method.

A. Fixed amount of dye and varied amount of Scandium(III)

With fixed ligand and variable cation concentrations, the application of Yoe-Jone mole-ratio method(32) is used. A series of solutions was prepared by adding increasing amount of 10^{-4} F. scandium solution(i.e., 1 , 2 , 3 , 4 , 5 ,6 , 7 , 8 ml.) to a fixed amount of 10^{-4} F. dye solution (i.e., 4 ml.) After adjusting the pH of the solution to 2.5 by the addition of 0.1F. Hydrochloric acid, the solution was diluted to 25 ml. The absorbance was measured at 630 nm. against the reagent blank. Results are shown in Table XI and Fig. II

Table XI

| ml.of 10^{-4} F.dye | ml.of 10^{-4} F.Sc(III) | mole fraction of scandium | Absorbance at 630 nm. |
|--------------------------|------------------------------|------------------------------|--------------------------|
| 4 | 1 | 0.20 | 0.150 |
| 4 | 2 | 0.33 | 0.303 |
| 4 | 3 | 0.44 | 0.440 |
| 4 | 4 | 0.50 | 0.555 |
| 4 | 5 | 0.56 | 0.555 |
| 4 | 6 | 0.60 | 0.555 |
| 4 | 7 | 0.63 | 0.555 |
| 4 | 8 | 0.67 | 0.555 |

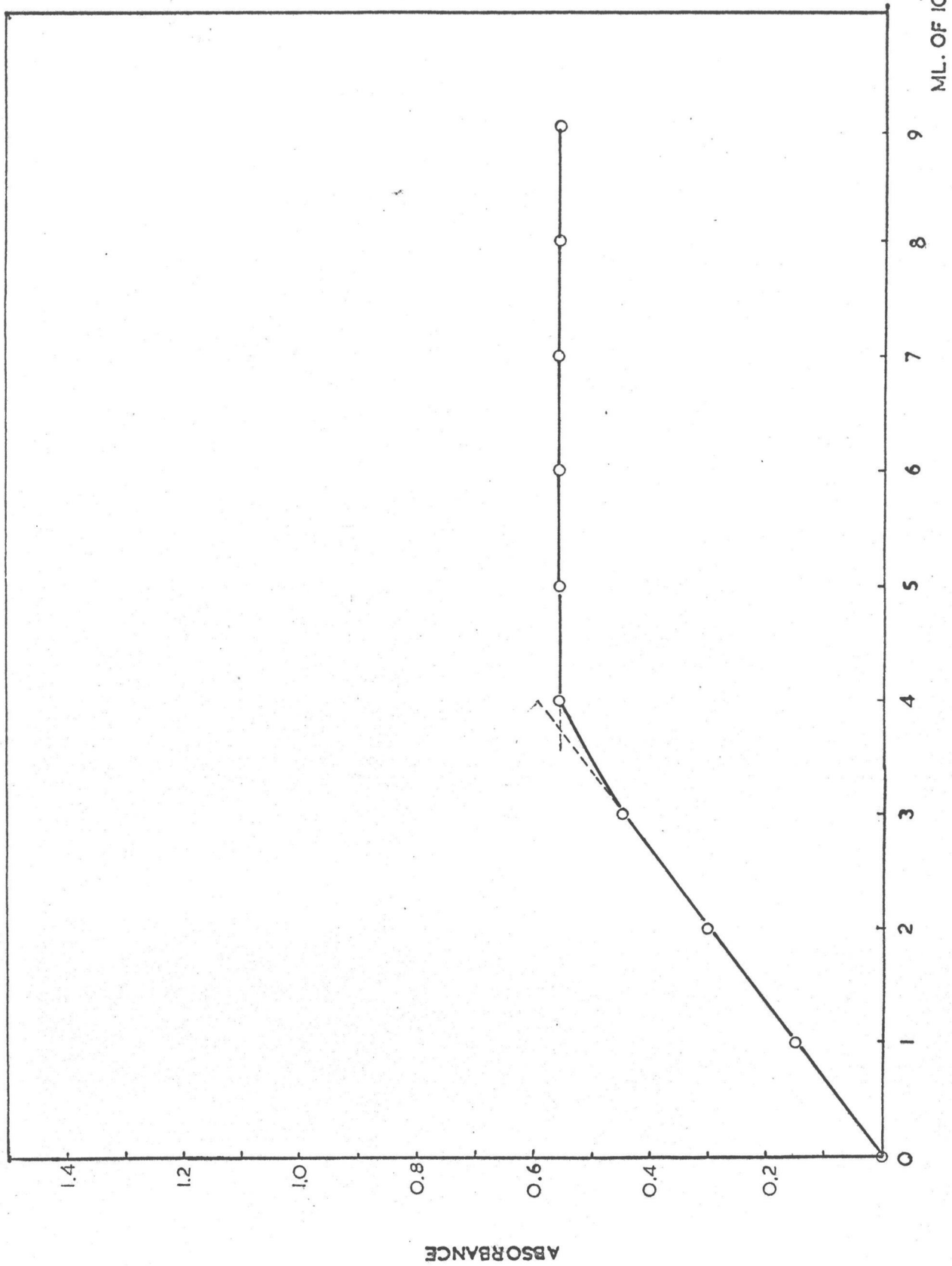


Fig. 11 Application of the mole ratio method of the scandium dye system.

[constant ligand concentration]

B. Fixed amount of scandium(III) and varied amount of dye

The solutions were prepared by adding the increasing amount of dye solution (that is 1,2,3,4,5,6,7,8,9,10,11,12 ml. of 10^{-4} F. solution) to a fixed amount of scandium solution (that is 4 ml. of 10^{-4} F. solution). The pH of solutions was adjusted to 2.5. The absorbance of solutions were measured at 630 nm. using water as the reference. Results are shown in Table XII, Fig 12. and Fig 13.

Table XII

| ml. of 10^{-4} F. dye | ml. of 10^{-4} F. Sc(III) | absorbance at 630 nm. |
|-------------------------|-----------------------------|-----------------------|
| 1 | 4 | 0.195 |
| 2 | 4 | 0.378 |
| 3 | 4 | 0.572 |
| 4 | 4 | 0.765 |
| 5 | 4 | 0.865 |
| 6 | 4 | 0.910 |
| 7 | 4 | 0.960 |
| 8 | 4 | 1.010 |
| 9 | 4 | 1.050 |
| 10 | 4 | 1.090 |
| 11 | 4 | 1.150 |
| 12 | 4 | 1.200 |

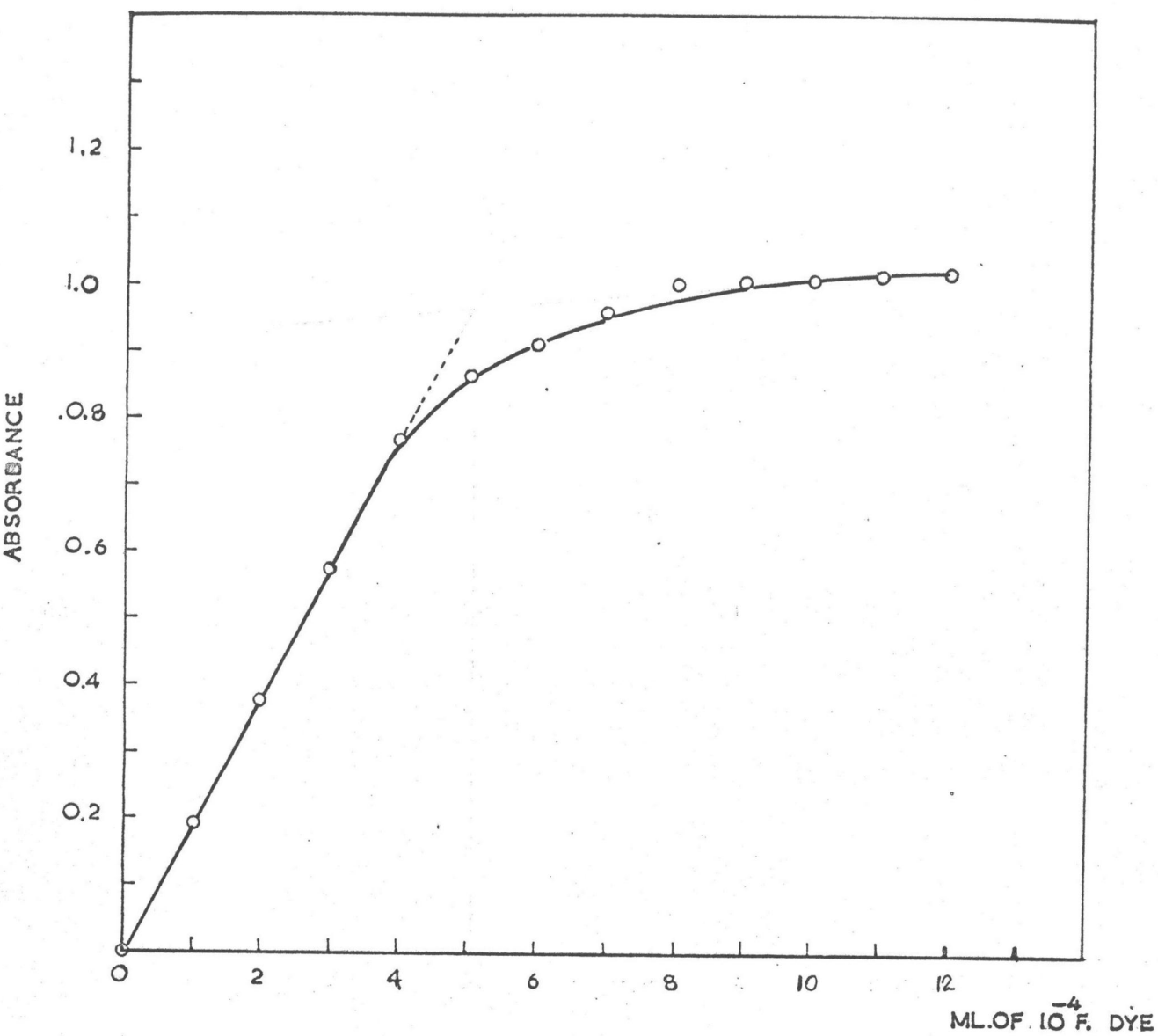
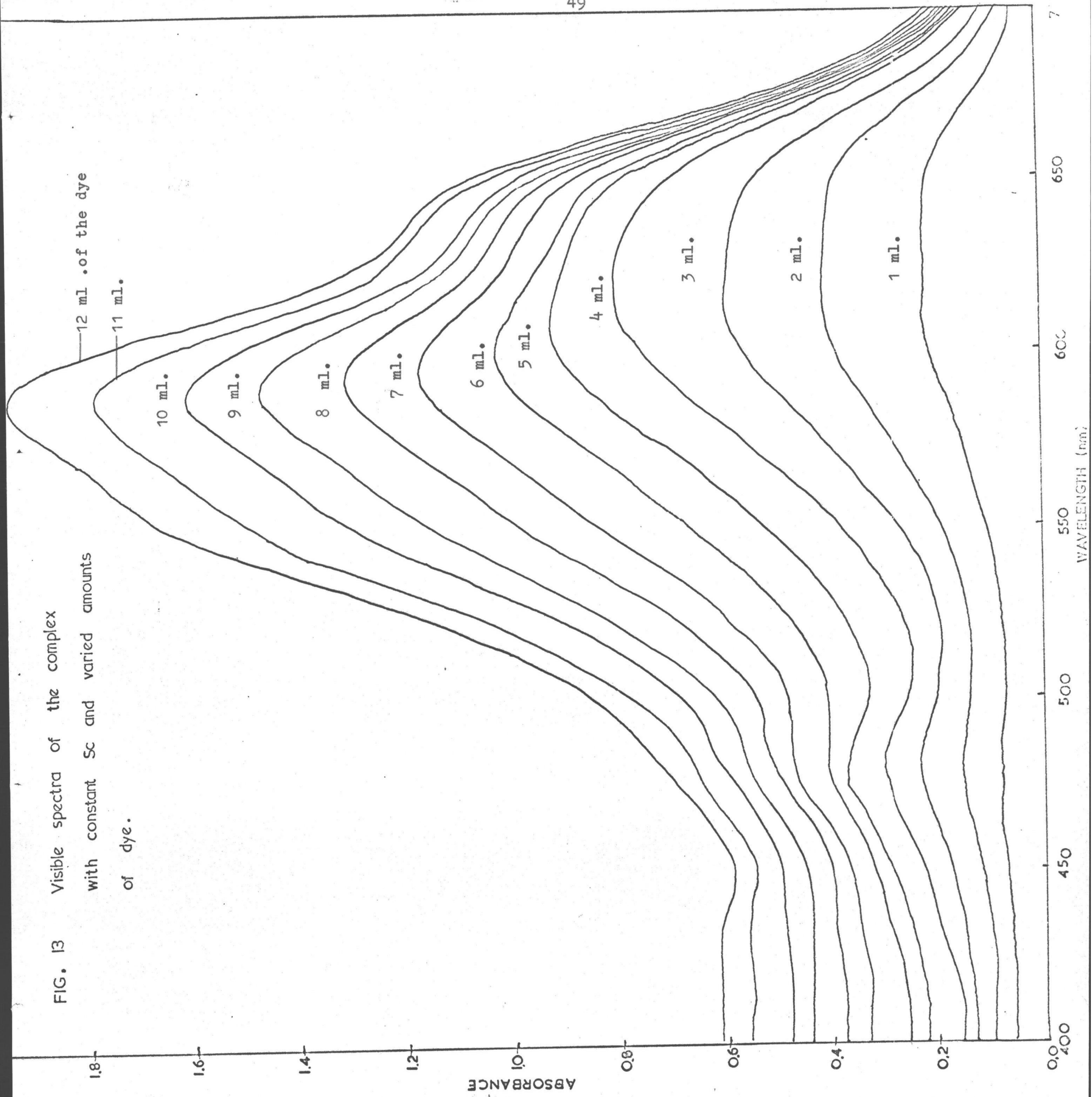


Fig. 12 Application of mole-ratio method to the scandium-dye system.
[constant cation concentration]

FIG. 13 Visible spectra of the complex
with constant S_c and varied amounts
of dye.



From Fig 12, it is confirmed that the scandium-dye complex of the type M:L = 1:1 formed.

2.5.3 Slope ratio method.(33)

A. Condition of excess metal concentration.

A series of solutions were prepared by adding amount of scandium solution (i.e., 14 ml. of 10^{-4} F. solution) to the varied amount of dye solution (i.e., 1, 2, 3, 4 and 5 ml. of 10^{-4} F. solution). The pH of each solution was adjusted to 2.5 by the addition of the appropriate amount of 0.1 F. hydrochloric acid and then diluted to 25 ml. with water. The absorbance of solutions were measured at 630 nm. using 1 cm. cell and water as a reference. Results are shown in Table XIII and Fig 14.

Table XIII

| ml. of 10^{-4} F. dye | ml. of 10^{-4} F. Sc(III) | absorbance at 630 nm. |
|-------------------------|-----------------------------|-----------------------|
| 1 | 14 | 0.193 |
| 2 | 14 | 0.393 |
| 3 | 14 | 0.572 |
| 4 | 14 | 0.753 |
| 5 | 14 | 0.964 |

B. Condition of excess dye concentration.

The method of the preparation of solution was exactly the same as described in A, except the fixed amount of 14 ml of 10 F.⁻⁴ dye solution and the varied amount of scandium solution were employed. The absorbance of each solution was measured at 630 nm. using 1 cm. cell and reagent blank as a reference. Results are shown in Table XIV and Fig. 14

Table XIV

| ml. of 10 F. ⁻⁴ dye | ml. of 10 F.Sc(III) ⁻⁴ | absorbance at 630 nm. |
|--------------------------------|-----------------------------------|-----------------------|
| 14 | 1 | 0.160 |
| 14 | 2 | 0.303 |
| 14 | 3 | 0.460 |
| 14 | 4 | 0.615 |
| 14 | 5 | 0.770 |

Calculation.

If the complex formed in the reaction



case 1.

$M \gg L$

from slope = $\frac{a \cdot b}{n}$

slope₁ = 0.18 = $\frac{ab}{m}$

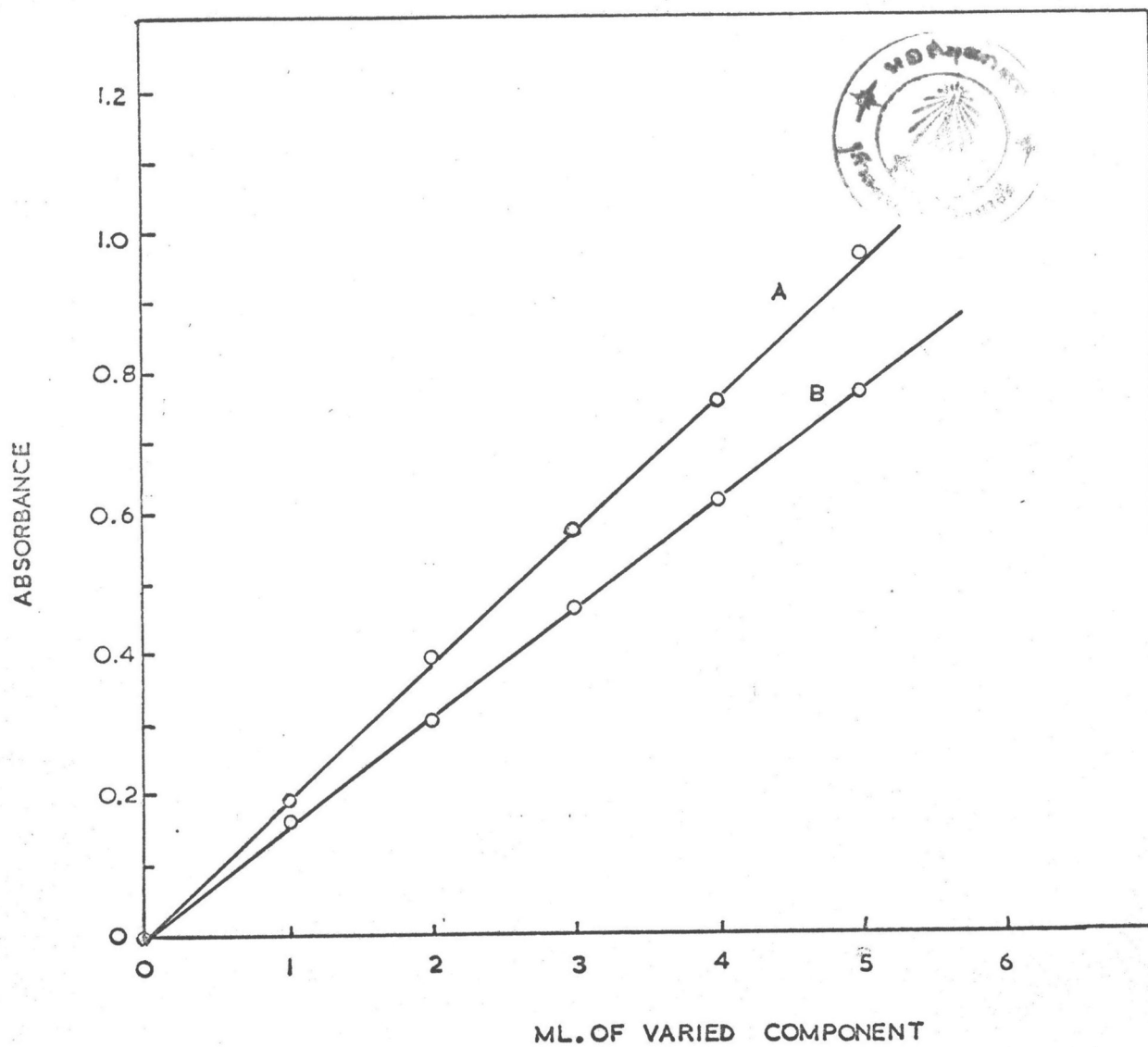


Fig. 14 Slope ratio method.

A $M \gg L$

B $L \gg M$

case 2 L >> M

$$\text{from slope} = \frac{a \cdot b}{n}$$

$$\text{slope}_2 = 0.155 = \frac{a \cdot b}{n}$$

A simple derivation base upon Beer's law and the assumption that the small quantities added in each case are quantitatively converted to equivalent amounts of $MnLm$, gives the relationship:

$$\frac{\text{slope 1}}{\text{slope 2}} = \frac{n}{n} = \frac{.18}{.155} = 1.16$$

Then the empirical formula is easily deduced to ML .

The study of the nature of scandium-dye complex by method of continuous variation, mole ratio method and slope ratio method reveal that the 1:1 mole ratio of scandium : dye complex is formed. This is also confirmed by the absorption spectra of the complex as shown in Fig. 15

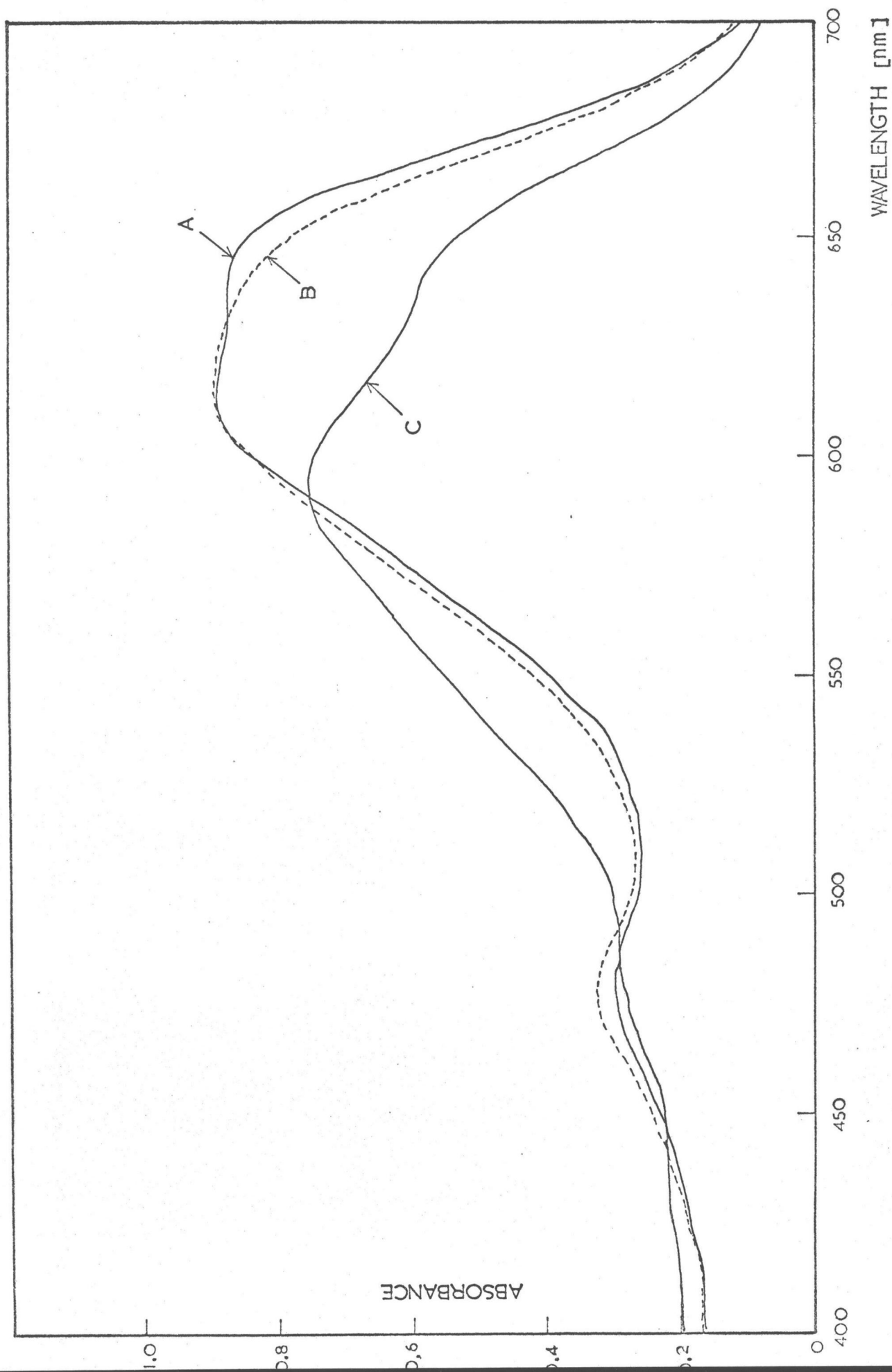


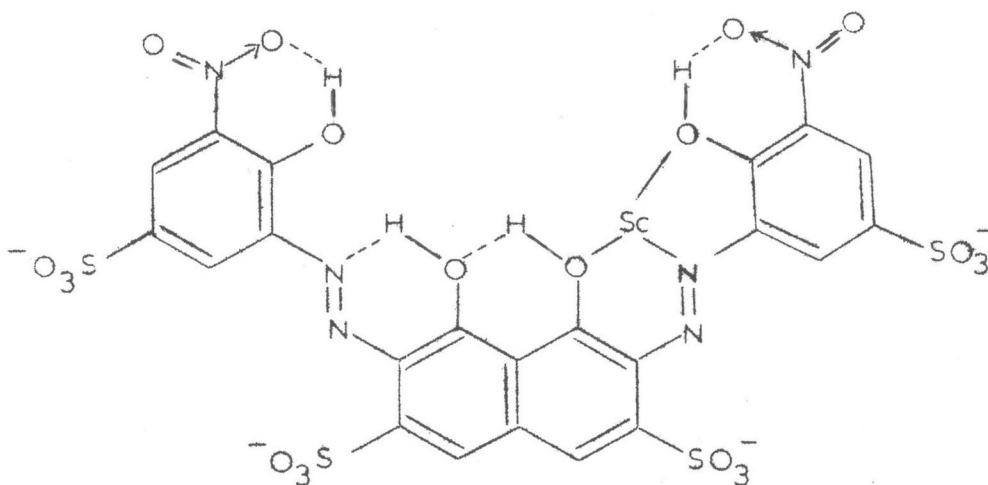
FIG. 15 The absorption spectra of the complex.

A M:L = 2:1

B M:L = 1:1

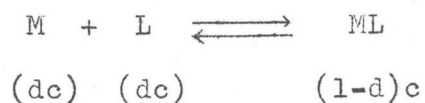
C M:L = 1:2

2.5.4 The proposed structure of the scandium-dye complex



2.5.5 Apparent stability of the scandium-dye complex

For the scandium-dye complex is in the type of ML, the formation reaction is as follows:



The apparent stability of this complex was calculated from the equation:

$$K = \frac{(1-d)}{d^2 c}$$

Where K is the apparent stability of the complex, c is the molar concentration of the reactant and d is the degree of dissociation defined by $d = \frac{A_m - A_s}{A_m}$ A_m is the maximal absorbance obtained from the extrapolation of the curve from Job's method of continuous variations and A_s is the absorbance at the stoichiometric molar ratio of metal to reagent.

From Fig.10, $A_s = 0.7$, $A_m = 0.745$, $c = 2 \times 10^{-5}$ F. then
 $d = 0.0604$ and

$$K = \frac{(1-0.0604)}{(0.0604)^2 \times 2 \times 10^{-5}}$$

$$K = 1.28 \times 10^7$$

2.6 Possibility of Using the Dye as an Indicator in a Complexometric EDTA Titration.

For the dye itself has a wine-red colour in the strong acid media (pH 2-2.5) while the scandium-dye complex, at the same medium, shows a blue colour. If the dye is used as an indicator in the complexometric titration between scandium solution and EDTA solution, at the end-point, the scandium is extracted from the scandium-dye complex by the EDTA and the colour of the solution will change from blue to wine-red (the scandium-EDTA complex has no colour). The end-point detection is studied by the following experiments.

2×10^{-2} F. Sc(III) solution and 10^{-2} F. EDTA solutions were prepared as primary standard solution, and 5 ml. of 10^{-2} F. Sc(III) was used in each time of the titration

5 ml of 10^{-2} F.Sc(III) was pipetted to a 250-ml beaker followed by 2 drops of 10^{-2} F.dye solution and 10 ml of water. The solution was adjusted to pH 2.0 by the addition of 0.1 M HCl. With constant stirring, the solution was titrated dropwise by 10^{-2} F. EDTA solution until the colour of the solution was changed from blue to wine-red. The amount of 10^{-2} F EDTA used was noted. The titration was repeated and result obtained is shown in Table XV.

Table XV

| No | 10^{-2} F.Sc(III) ml | 10^{-2} F. EDTA used ml | ng. of Sc(III) theoretical value | ng. of Sc(III) found |
|----|---------------------------|------------------------------|-------------------------------------|-------------------------|
| 1 | 5 | 9.90 | 4.5 | 4.545 |
| 2 | 5 | 10.00 | 4.5 | 4.500 |
| 3 | 5 | 10.00 | 4.5 | 4.500 |
| 4 | 5 | 9.80 | 4.5 | 4.590 |
| 5 | 5 | 10.00 | 4.5 | 4.500 |
| 6 | 5 | 10.00 | 4.5 | 4.500 |

From the visual observation, the colour of the end-point changes with in one drop of the titrant. From the calculation, the result shows that this dye can be used as an indicator in this titration system with reasonable accuracy .

2.7 Conclusion

Studies of the properties of 1,8-dihydroxy-2,7-bis(2-hydroxy-3 nitro-5-sulpho-1-phenylazo)-naphthalene-3,6-disulphonic acid, reveal that this dye has a metallochromic indicator property. The work is carried out with the emphasis on the uses of this dye as a reagent for the spectrophotometric determination of scandium under the optimal working conditions. The complex formed has the combination ratio of scandium to the dye which is found experimentally to be 1 to 1. The proposed structure of the scandium-dye complex in aqueous medium at pH 2.5 is shown on page 55. At very low pH value the hydrogen ion in the solution will suppress the ionization of the H^+ ion from -OH group but when the pH is increased, the H^+ ion can dissociate from the resonance system causing a colour change (wine red \rightarrow mauve blue \rightarrow indigo). At medium acidic solution, the H^+ ion ionizes from the 2-hydroxy phenylazo part and at higher pH, from the 1,8-dihydroxy naphthalene nuclei. At pH 2.5, the complex is formed, the scandium ion would enter the space between orthohydroxy and the azo nitrogen of the dye. The lone-paired of electrons of the oxygen and nitrogen are donated to the scandium ion. The complex is formed in this mode because of the characteristic of the o-hydroxy azo dye. The scandium may not form the coloured-complex with the dye molecule through the peri-position of the chromotropic acid nucleus since the scandium ion is rather voluminous in the aqueous medium. The possible structure of the complex may be proposed as appeared in the page.55

The conditional formation constant for the complex at pH 2.5 at 25°C calculated from the curve of the continuous variation method is 1.28×10^7 . The spectrophotometric determinations of scandium show promising reproducibility with coefficient of variation $\pm 1.3\%$ solution containing $0.36 \mu\text{g}$ of scandium (III) per ml without interfering ions or masking agents. The sensitivity of the reaction expressed by Sandell's notation (34), $n \frac{M}{\epsilon}$ (Where M is the molecular weight in grams of the compound expressed in term of elements, n is the number of atoms of the element in a molecule of a compound and ϵ is the molar absorptivity of the compound) is $0.0012 \mu\text{g}$. of scandium(III) per cm^2 for $\log \frac{I}{I_0} = 0.001$. The molar absorptivity of the 1 to 1 complex at 630 nm. is 3.75×10^4 .

In the study of the effect of various interfering ions, results show that Cu(II), Ni (II), Co (II), Pb(II), Al(III), Mo(IV), Hg(II), UO₂ (II), Cr(III), Th(IV), Fe(II), La(III) interfere seriously when the interfering ion is present 100 moles excess over that of scandium and the effect is decreased as the amount of the diverse ion decreases, that is, Mn(II) does not interfere within the 50 moles excess. If the ratio of the interfering ion to scandium is reduced to 10, it is appeared that Hg(II), Ba(II), Sr(III) do not interfere and Mg(II), Pb(II), Cr(II) do not interfered if the ratio is 1, but Na(I), Ca(II), citrate SO₄⁻², NO₃⁻, et, acetate, PO₄⁻³ do not interfere even the molar ratio is equal to 100.

Usually an undesirable constituent can interfere either because of its own peculiar optical properties or because it can undergo chemical reaction with the sought-for constituent {scandium (III)}, the manifestations of these modes of interference may include fading (such as in the case of F^-), extraneous absorption (La (III), Th(IV), Cu(II), Cr(II), $Fe(II)$ etc.) Turbidity (Sn(II)).

A variety of techniques may serve to reduce or eliminate the interfering effect of the undesired constituents such as a physical separation of scandium from the undesired constituent but it is not always as satisfactory in practice as in theory because of the increment of error. Other means is the conversion of the undesirable constituents by chemical means into species that do not interfere. It is generally preferred to physical separation. Many types of reactions are commonly employed. Oxidation-reduction and complexations prove particularly effective for inorganic systems.

By the application of the above techniques, the interfering effect of such diverse ions may be eliminated or at least, reduced, this proposed method will become a suitable one.

Considering the sensitivity of the method and comparing with the methods using some other azoic compounds, This new reagent gives a higher molar absorptivity than all others except that of 4-(2-Thiazolylazo)resorcinol. This method has however some advantages over others, namely, the very stable complex is formed, the procedure is so simple and the calibration curve is reproducible and reliable.

During the course of this work, this dye was used as an indicator in the direct visual complexometric titration of scandium (III) with standard EDTA solution. The pH of the titration medium was 2.0. At the beginning the indicator combined with the trace amount of scandium (III) exhibited a blue colour of the scandium-dye complex,



wine red

blue

at the end-point, EDTA solution extracted the trace scandium from the complex form and the free form of the indicator was left the colour was therefore changed from blue to wine red (at low pH value the dye itself shows a wine-red colour). The final concentration of the indicator is approximately 10^{-5} F. The end-point is rather sharp this may be due to the high molar absorptivity of the complex and the shade of the colour change is easily distinguished. From the visual observation, at the end-point, the colour change within one or two drops of 10^{-2} F. EDTA solution. So this dye should be recommended as a potential metal indicator in the direct visual complexometric titration of scandium (III) in strongly acidic solution.

As described above, it can be seen that this dye, 1,8-dihydroxy-2,7-bis(2-hydroxy-3-nitro-5-sulpho-1-phenylazo)-naphthalene-3,6-disulphonic acid, is recommended to be a sensitive metallochrome in the spectrophotometric determination and visual direct complexometric titration for scandium.