THE pH AND CONCENTRATION EFFECT IN THE $Ce^{(III)}$-ALIZARIN COMPLEXONE-FLUORIDE SYSTEM

By

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ALIZARIN COMPLEXONE-FLUORIDE SYSTEM

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES (Continued)

LIST OF FIGURES

LIST OF FIGURES (Continued)

CHAPTER I

INTRODUCTION

Alizarin complexone (1,2-Dihydroxyanthraquinone-3-ylmethyl amine-N,N-diacetic Acid) which is yellow below a pH of 6, forms a wine-red chelate with $Ce^{(III)}$ metal ion, this red chelate gives a specific color reaction with the fluoride ion. No other anion is found to react similarly, and among the rare earths available, only Lanthanum and Prasedymium give the reaction.

The formation of blue color by the fluoride ion furnishes a sensitive method for its spectrophotometric determination. By this method a wide range of fluoride ion concentration (0.1 - 160 ppm) can be determined if the pH of the solution is 5-5.2, the optimum pH range for this method.

In this thesis the effect of pH on the $Ce^{(III)}$-Alizarin complexone chelate and its ternary fluoride complex was investigated in both the visible and the ultra-violet regions of the spectrum.

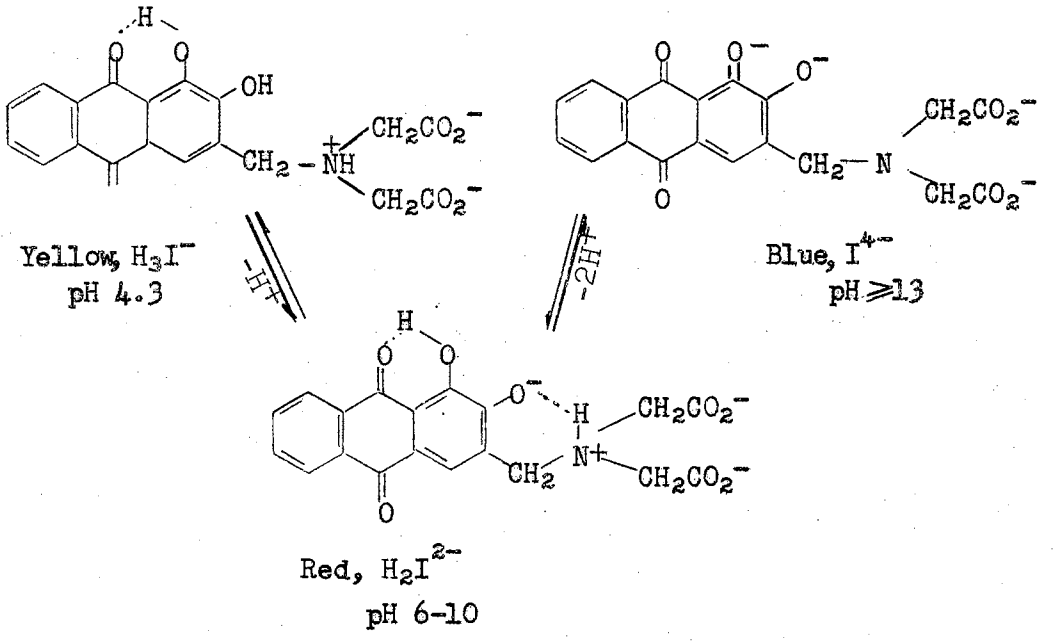
An aqueous medium was chosen in this work because the ionization constant of hydrogen fluoride was known in this medium. No values of this constant were available for 20% acetone or acetonitrile medium where a higher stability of the complex and sensitivity of the reaction would have been achieved. The value of the ionization constant was used in calculating free fluoride ion concentration at maximum absorbance for different fluoride ion concentration and different pH values.

REVIEW OF LITERATURE

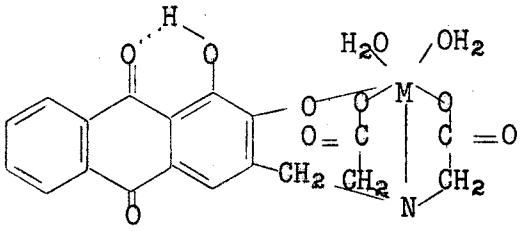
The formation of the blue fluoride complex by the reaction of fluorine and $Ce^{(III)}$-Alizarin complexone chelate was developed by Belcher, Leonard and West (1). This test was the first color test for the detection of fluoride ion which produced color rather than bleaching a colored metal chelate by the formation of a colorless metal-fluoride complex.

Belcher, Leonard and West (2) constructed a calibration curve for fluoride ion concentration using solutions buffered with acetate to a pH of 4.3 and measuring absorbance at 610 mμ against the reagent. The curve was linear over the range of 8 to 35 micrograms of fluoride per millilitre but the projection did not pass through the origin.

Leonard and West (3) gave an equation for the protolysis mechanism or an acid base reaction of Alizarin complexone as shown below: (where I = the complex ion)



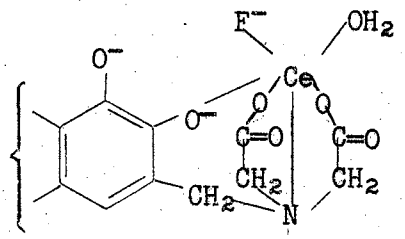
The formation of metal chelate (3) occurs through the two acetic acid groups, the 2-hydroxy group, and the nitrogen atom as shown in the structural formula:



Typical metal chelate of Alizarin complexone

This attack on the 2-hydroxyl group would explain the close similarity between the absorption spectra of the metal chelate and the H_2I^{2-} form of the metal-free reagent at pH 6-10.

The blue fluoride complex gave an absorption maximum at 567 mμ which agrees with that of the metal-free reagent at pH 12.4 (I^{4-}), also the shape of the curves are almost similar.



Ternary Fluoride Complex

The nature of the ternary fluoride complex formed was studied by Leonard and West (3) by using the Job's method of continuous variation. They used 1:1 $Ce^{(III)}$-Alizarin complexone and found that a 1:1 fluoride complex was formed.

They also found that when one molar proportion of fluoride ion was

added to a 1:1 $Ce^{(III)}$-Alizarin complexone chelate, the solution gave maximum color intensity at 567 mμ, adding another molar proportion of fluoride did not change the wavelength of maximum absorption. When a large excess of fluoride was added, precipitation of $Ce^{(III)}$ as its fluoride occurred leaving a yellow solution of the metal-free reagent. Specific action of fluoride ion was explained as due to the strong electronegative properties of the atom.

Belcher and West (4) found that the optimum sensitivity of fluoride reaction with $Ce^{(III)}$-Alizarin complexone chelate occurred at pH 5-5.2. They recommended that this method not be operated beyond a pH range of 4-6. Above pH 6 hydrolysis of the fluoride complex occurred with replacement of the fluoride ion by a hydroxyl ion.

High concentration of fluoride ion could be analyzed if the concentration of the $Ce^{(III)}$-reagent was increased. A 10^{-2} M fluoride solution could be analyzed using a pH 5-5.2 while at pH 4.3 precipitation occurred with 5×10^{-3} M solutions.

Jeffery and Williams (5) constructed a three dimentional continuous variation diagram for the system F^- + $Ce^{(III)}$ + Alizarin complexone and found that a maximum occurred indicating a composition ratio of 4:4:5.

Yamamura, Wade and Sikes (6) explained the effect of acetate buffer. Higher concentration of buffer decreased the net absorbance. A secondary effect of the buffer was to promote the reaction of fluroide with the $Ce^{(III)}$-Alizarin complexone chelate. They suggested that at least two positions of the $Ce^{(III)}$-Alizarin complexone were occupied by the acetate ion and not by the water molecules.

They observed that in the presence of acetate ion, the formation

of the blue color was rapid, possibly because of the easy replacement of the acetate ions by the fluoride ions. In the absence of the acetate ions, the blue color formed noticeably slower and less completely.

Leroy Maden (7) stated that when the amount of fluorine in the sample was too great, the purple color of the complex bleached to an orange or even yellow. If the pH was raised to about 5.5 by the addition of NaOH, the purple color appeared again. Because of the dependance of the reaction on the pH, he reported that the reaction was a function of the hydrogen fluoride concentration instead of the fluroide ion concentration.

In this thesis the effect of pH on the system was investigated and an explanation of its effect on the reactions of fluoride ion with $Ce^{(III)}$-Alizarin complexone chelate is given.

CHAPTER II

EXPERIMENTAL

Reagents and Solutions

0.0176 M Alizarin Complexone Solution.--Suspend 0.043 grams of the reagent in 50 ml of water. Dissolve with 0.25 ml of concentrated ammonium hydroxide. Add 0.25 ml of glacial acetic acid and dilute to 100 ml. This solution is stable for about a month under normal laboratory conditions.

The Alizarin complexone reagent was obtained from K & K Laboratories, Inc., Plainview, New York.

0.0167 M Cerium Nitrate Solution.--Dissolve 3.6260 grams of $Ce(NO_3)_3 \cdot 6H_2O$ in water and dilute to 500 ml with water.

pH 4 Buffer Solution.--Dissolve 60 grams of sodium acetate trihydrate in 200 ml of water. Add 115 ml of glacial acetic acid and dilute to 1 litre.

Standard Fluoride Solution.--Dissolve 2.210 grams of oven dried reagent grade sodium fluoride (Baker Analyzed Reagent, 99.9% NaF.) in 1 litre of water. This solution contains 1 mlg.F^-/ml of solution. 25 ml of this solution was pipeted and diluted to 500 ml with water to give a solution which contains 50 µg/ml F^-, and transferred immediately to a polyethylene bottle for storage.

Composite Solution Used in the Visible Range.--Mix in order and

with swirling 68 ml of the buffer solution, 10 ml alizarin complexone reagent and 10 ml of cerium nitrate solution. Dilute to 500 ml with water and transfer to a polyethylene bottle.

This solution should be stable for about four to five days if protected from heat and direct sunlight.

Composite Solution Used in the Ultra-Violet Range.--Prepare as above only use 5 ml of each alizarin complexone and cerium nitrate solutions instead of 10 ml, make up the difference in volume by adding water.

Only deionized water was used in the preparation of reagents and solutions.

Apparatus Used

Spectrophotometers.--The Beckman DB Spectrophotometer was used with a strip chart recorder. The tungsten lamp used in the visible region and the hydrogen lamp in the U.V. region. The DB model was used only in the preliminary work. Battery-operated Beckman model DU spectrophotometer with a photomultiplier was used with a Tungsten lamp and a constant slit width in the visible region and a hydrogen lamp in the ultra-violet region.

Cells.--10 mm. matched Beckman Silica cells were used for both visible and U.V. regions. One cell was used for solutions and the other for the blank throughout the work and they were kept in the same relative position while taking the absorbance readings to minimize the error.

pH Meter.--A Beckman expanded scale pH meter with a glass electrode was used for pH adjustments.

Glass and Plastic Ware.--All glassware used was Pyrex, volumetric glassware met A.C.S. requirements for accuracy. Nalgene polyethylene bottles were used for storing the solutions.

Computers.--All computer work was done on an IBM 7040 at Oklahoma State University Computer Center.

Preparation of Solutions

Solutions Used in the Visible Region.--Solutions used in this region were made to have 0, 2, 5, 10, 15 and 20 μg/ml F^-. This was done by pipeting the volume needed of 50 μg/ml F^- standard solution into a 50 ml volumetric flask and then adding 15 ml of the composite reagent made for the visible region.

Each of the above solutions was used at five different pH values. The pH was adjusted to the required value by transferring the solution to a small beaker and with the use of a magnetic stirrer and a pH meter, the pH was adjusted by using 1 N solutions of HCl or NaOH as required in a medicine dropper and let the tip just touch the solution, the pH will change by diffusion. This method of pH adjustment insures a minimum change in volume. The pH values used were 4.0, 4.5, 5.0, 5.5 and 6.0.

Solutions Used in the Ultra-Violet Region.--Solutions used in this region were prepared as those in the visible region except using the composite reagent made for the U.V. region.

Solutions in this region are made to contain 0, 2, 5, 10 and 15 μg/ml total fluoride ion concentration.

Absorbance readings for all solutions were taken at least after 30 minutes of make-up and not more than one day.

Deionized water was used as a blank.

Stoichiometry of all solutions prepared are given in Tables I and II.

Procedure

Absorbance data were taken on a DU-Spectrophotometer using a Tungesten lamp in the visible region and a mercury lamp in the ultra-violet region. In the visible, data were taken with a constant slit width of 0.02. In the ultra-violet the slit was increased very slightly as the wavelength was decreased to give the sensitivity required.

Absorbance readings were taken at least 30 minutes after preparation of solutions and not more than 24 hours. The pH of the solution was adjusted to the required value on a pH meter as described in the preparation of solutions.

In the visible region readings were taken from 650 mμ to 400 mμ by varying the wavelength by 10 mμ at a time. In the ultra-violet region absorbance readings were taken from 350 mμ to 230 mμ by varying the wavelength by 5 mμ at a time.

The same procedure was used for all solutions prepared.

Deionized water was used as a blank.

For each solution prepared, absorbance data were arranged in a matrix form with 5 different pH values and 26 wavelengths in the visible and 15 wavelengths in the ultra-violet.

The same data were used in the determination of rank of matrix, in the three dimensional plots and were also plotted as a function of wavelength and pH.

TABLE I

STOICHIOMETRY OF SOLUTIONS USED IN THE VISIBLE

Total F^- g/ml	Total F^- M x 10^{-4}	1:1 $Ce^{(III)}$-Alizarin Complexone M x 10^{-4}
0	-	1.00
2	1.052	1.00
5	2.630	1.00
10	5.26	1.00
15	7.89	1.00
20	10.52	1.00

TABLE II

STOICHIOMETRY OF SOLUTIONS USED IN THE ULTRA-VIOLET

Total F^- g/ml	Total F^- M x 10^{-4}	1:1 $Ce^{(III)}$-Alizarin Complexone M x 10^{-4}
0	-	0.502
2	1.052	0.502
5	2.630	0.502
10	5.26	0.502
15	7.89	0.502

CHAPTER III

RESULTS AND DISCUSSION

Solutions with no Fluoride Ion

1:1 $Ce^{(III)}$-Alizarin Complexone in the Visible Region.--Absorbance readings were plotted versus wavelength in Fig. 1. The absorbance matrix is given in Table VI. By increasing the pH by .5 units at a time, the maximum absorbance values increased.

At pH 5, the wavelength of maximum absorbance was at about 520 mμ. As the pH was increased a shift of wavelength toward higher values was observed. The wavelength of maximum absorbance at pH 6 was at 540 mμ.

At 480 mμ an isobestic point was observed.

1:1 $Ce^{(III)}$-Alizarin Complexone in the Ultra-Violet Region.--Absorbance versus wavelength were plotted in Fig. 2. The absorbance matrix is given in Table XIII.

The wavelength of maximum absorbance at pH 4 was about 263 mμ, while at pH 5.5 it shifted to 268 mμ.

Solutions with Fluoride Ion in the Visible Region

2 μg/ml F^-.--This solution was 1.00×10^{-4} M in $Ce^{(III)}$-Alizarin complexone and 1.052×10^{-4} M total fluoride ion concentration. The absorbance matrix is given in Table VIII.

Absorbance readings were plotted versus wavelength in Fig. 3. The

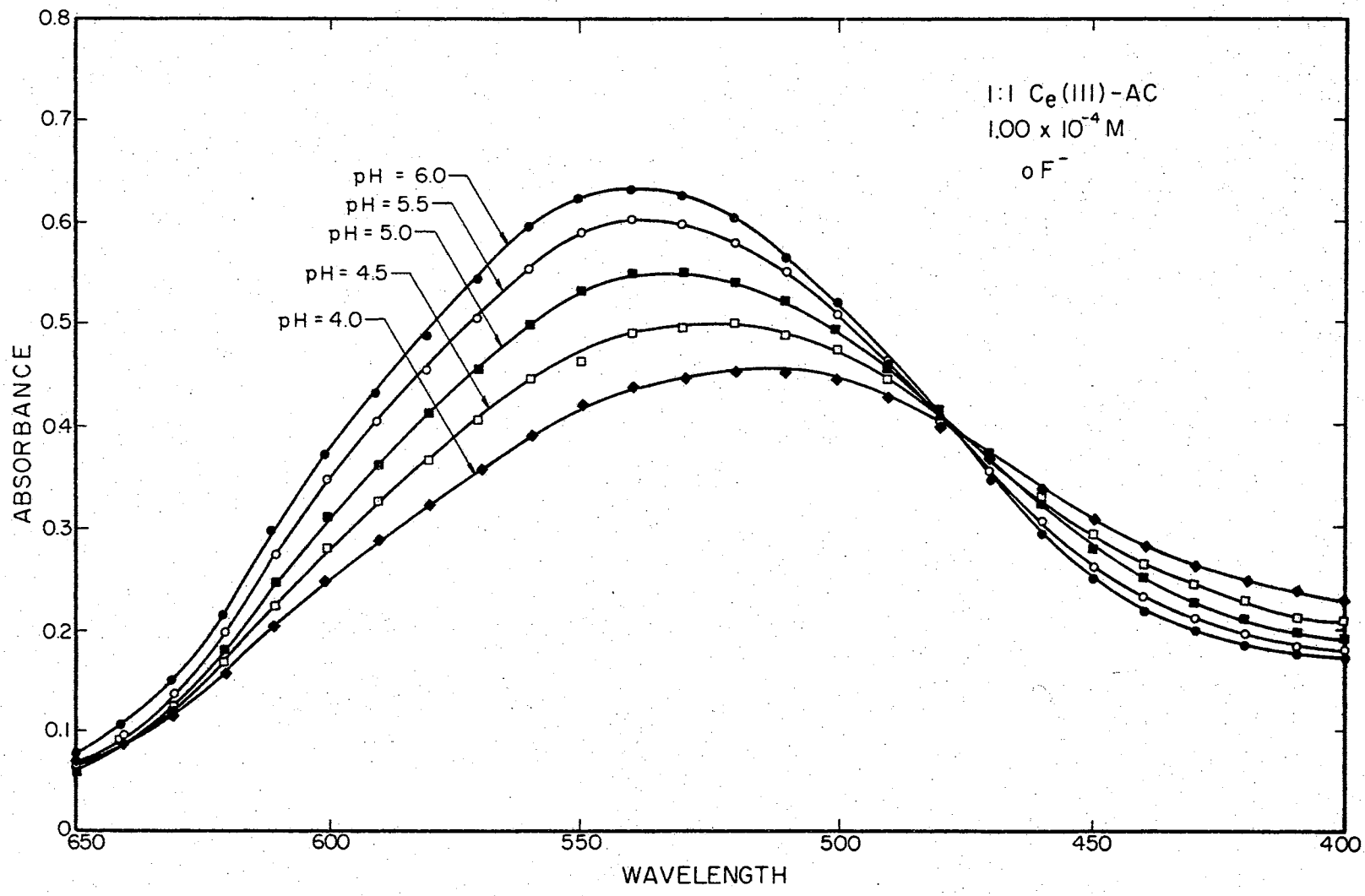


Figure 1. Plot of Absorbance vs. Wavelength for 1:1 $Ce^{(III)}$-Alizarin Complexone, Visible.

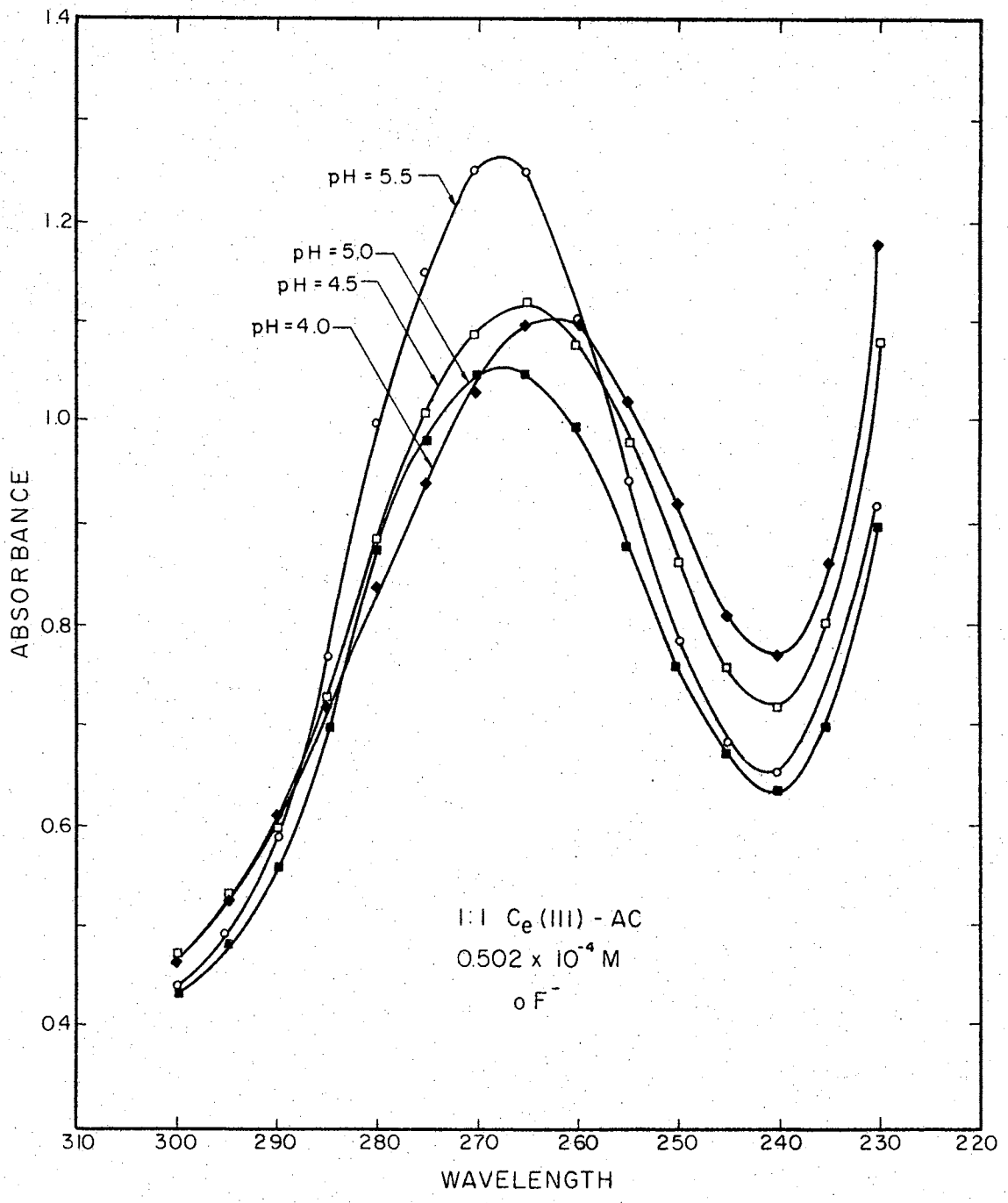


Figure 2. Plot of Absorbance vs. Wavelength for 1:1 $Ce^{(III)}$ - Alizarin Complexone in the UV.

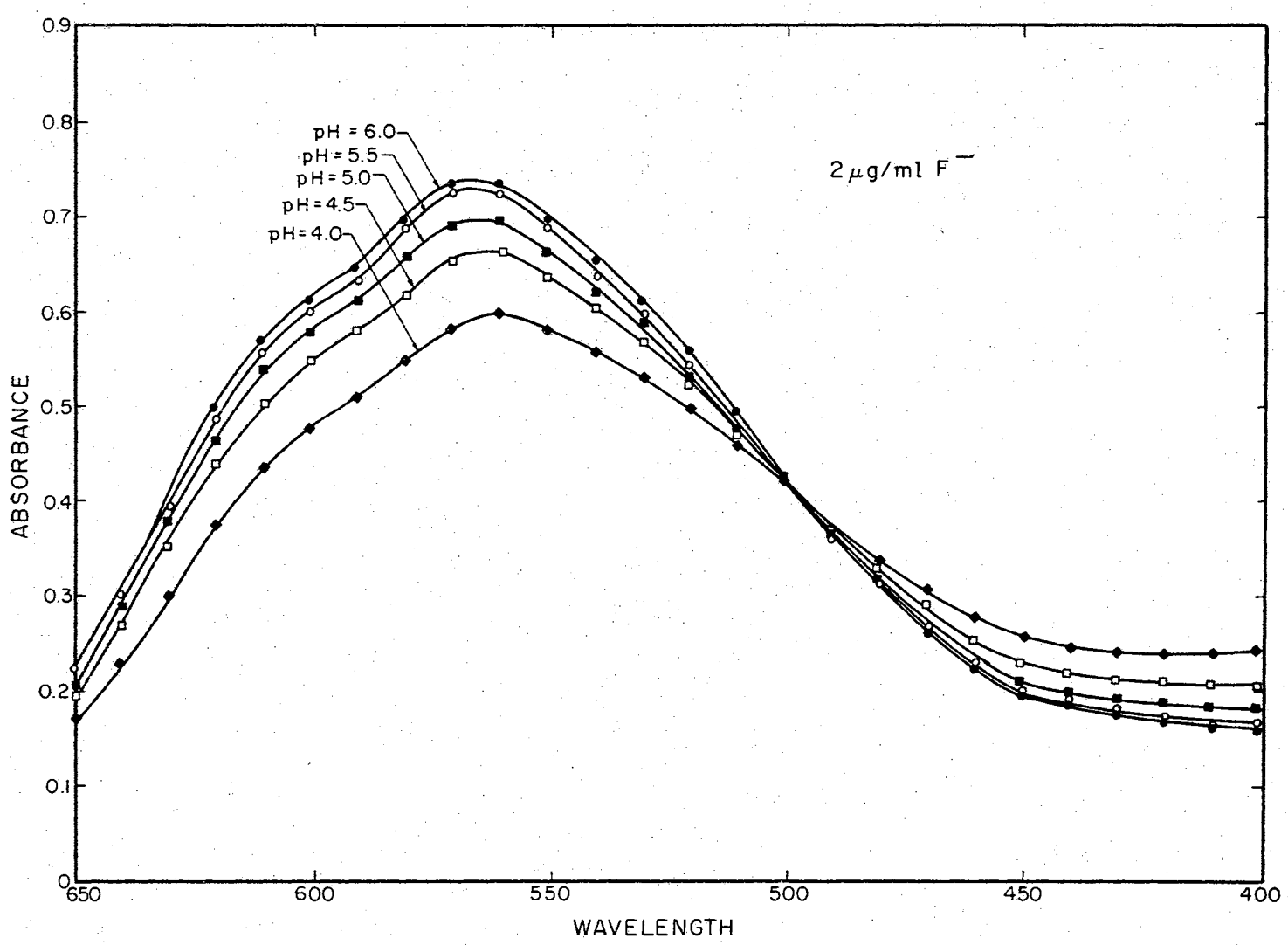


Figure 3. Plot of Absorbance vs. Wavelength for 2 μg/ml F^- in the Visible.

maximum absorbance increased by increasing the pH value. A much smaller increase in maximum absorbance occurred by changing the pH from 5.5 to 6 compared to the change of absorbance value when the pH was changed from 4.0 to 4.5 or from 4.5 to 5.0.

Wavelength of maximum absorbance was found to be between 560 and 570 mμ. An isobestic point was observed at 500 mμ. A shoulder at about 590 mμ was also observed for all the pH values.

20 μg/ml F^-.--This solution was 1.00×10^{-4} M in $Ce^{(III)}$-Alizarin complexone and 10.52×10^{-4} M in total fluoride ion concentration. The absorbance matrix is given in Table XII.

Absorbance plotted versus wavelength is given in Fig. 4. The wavelength of maximum absorbance was also between 560-570 mμ and did not change by increasing the fluoride ion concentration.

Maximum absorbance values increased by increasing the pH of solution. At this high concentration of total fluoride ion, changing the pH had a much larger effect on the value of maximum absorbance.

An isobestic point was also observed at 500 mμ. But here at pH 4 no shoulder at 590 mμ was observed. By increasing the pH the shoulder reappeared and was very much pronounced at pH 5. At the lower pH values the shape of the curve was similar to that of solutions with no fluoride ion, even the color of solution was reddish, which could mean that very small amount of the fluoride ion was present in the blue complex form. As the pH of the solution was increased, the blue color appeared again so did the shoulder in the curve. This could also be explained that as the pH was increased, more of the fluoride ion was being complexed.

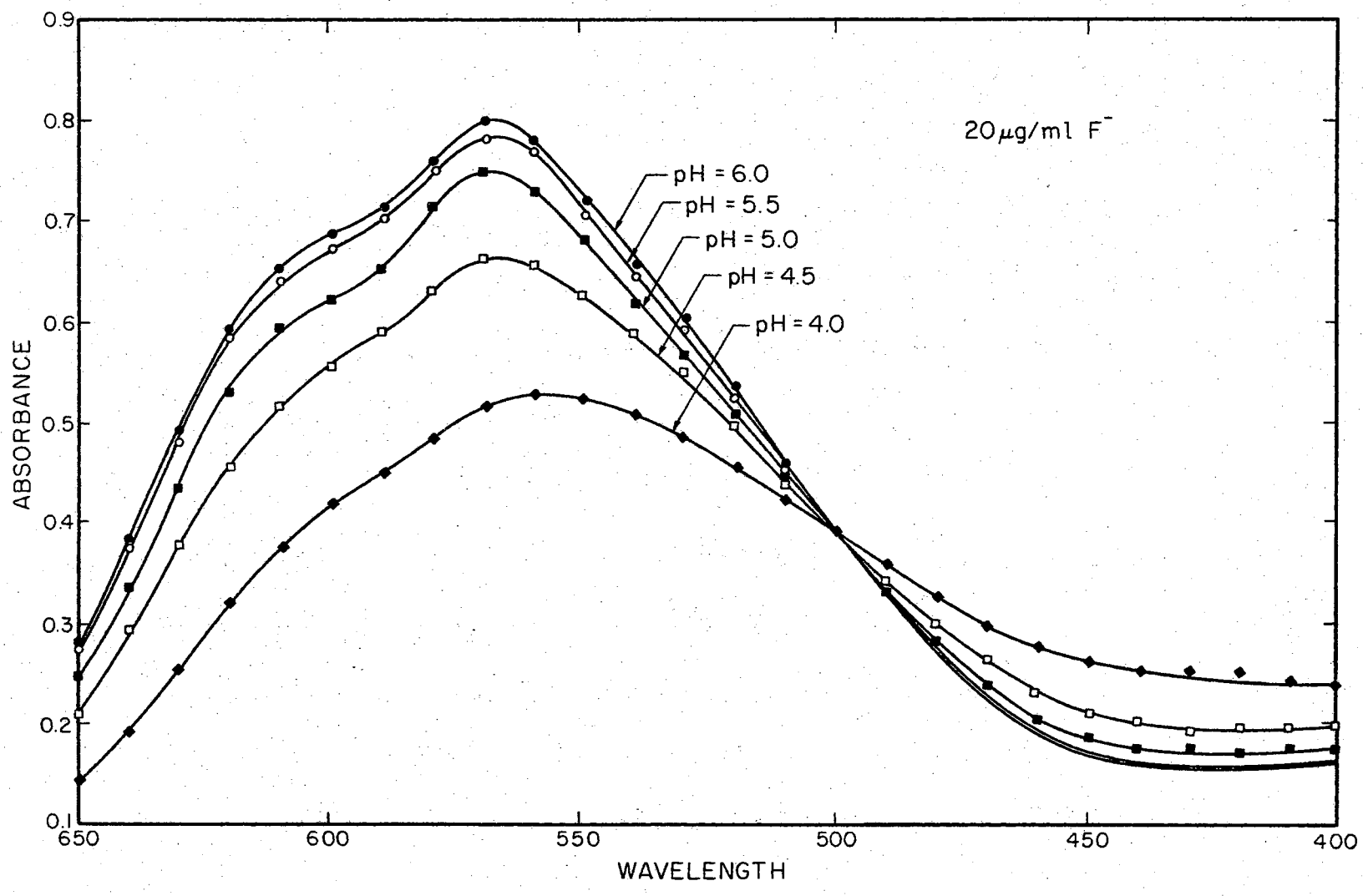


Figure 4. Plot of Absorbance vs. Wavelength for 20 μg/ml F^- in the Visible.

Solutions with Fluoride Ion in the Ultra-Violet Region

2 μg/ml F^-.--This solution was .502 x 10^{-4} M in $Ce^{(III)}$-Alizarin complexone and 1.00 x 10^{-4} M in total fluoride ion concentration.

The absorbance matrix is given in Table XIV.

Absorbance was plotted versus wavelength in Fig. 5. Wavelength of maximum absorbance was about 275 mμ and an isobestic point was at 265 mμ. A minimum absorbance or a dip was observed at about 245 mμ.

Increasing the pH, absorbance values increased at the maximum and decreased at the minimum.

10 μg/ml F^-.--This solution was .502 x 10^{-4} M in $Ce^{(III)}$-Alizarin complexone and 5.26 x 10^{-4} M in total fluoride ion concentration. The absorbance matrix for this solution is given in Table XVI.

Absorbance was plotted versus wavelength in Fig. 6. Wavelength of maximum absorbance was again at 275 mμ and did not change when the fluoride ion concentration was changed. An isobestic point at 265 mμ and a dip at 245 mμ was also observed.

Maximum absorbance increased by increasing the pH from 4.0-5.0 and did not change much by changing the pH from 5.0 to 5.5.

Plots of Absorbance Versus pH

Visible Region.--A plot of absorbance values at 560 mμ versus pH is given in Fig. 7.

At a low concentration of fluoride ion (2 μg/ml), increasing the pH gave an increase in the absorbance. Changing the pH from 4 to 5 gave a linear increase in absorbance.

At a higher concentration of fluoride ion (20 μg/ml), changing the

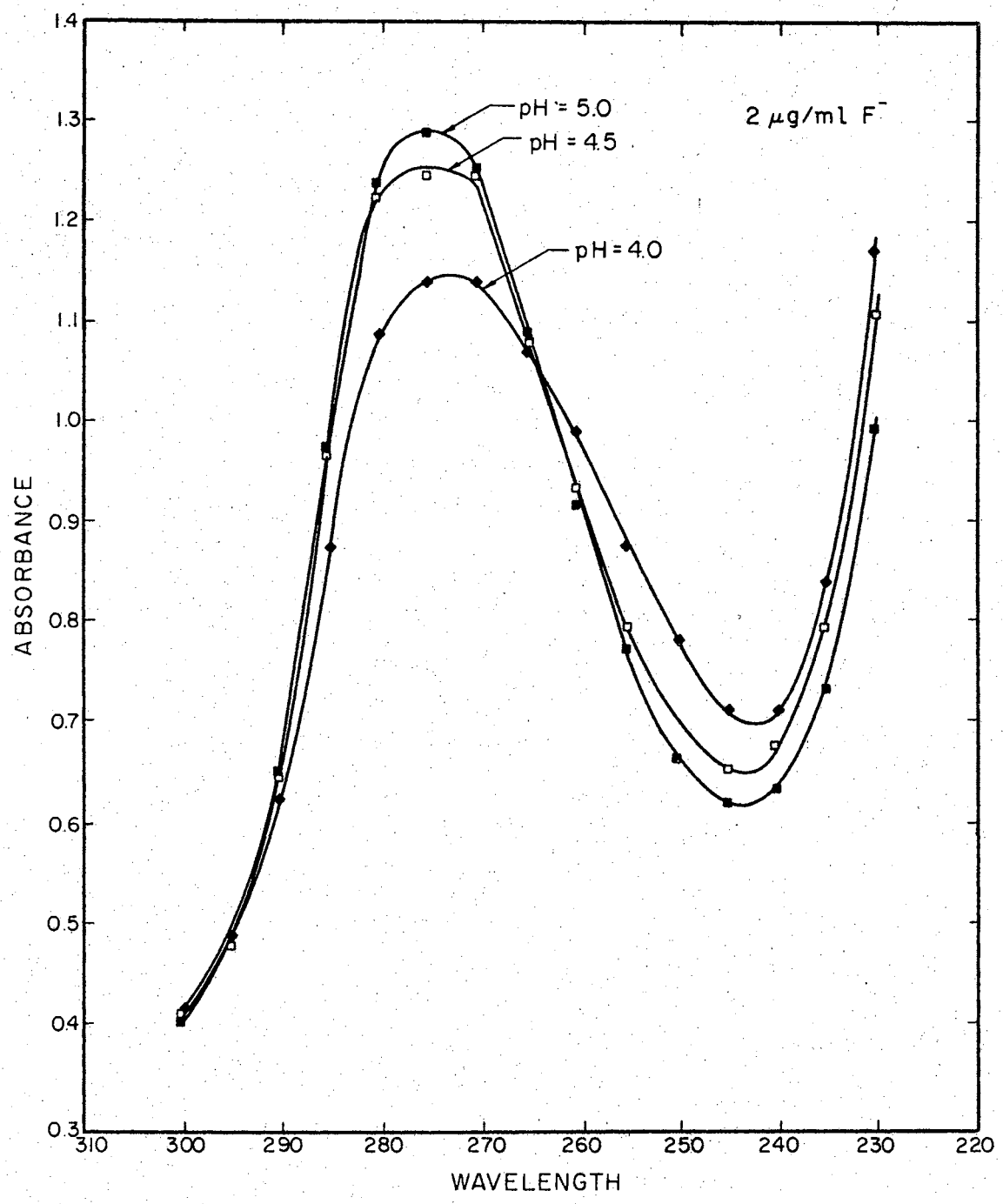


Figure 5. Plot of Absorbance vs. Wavelength for 2 µg/ml F^- in the UV.

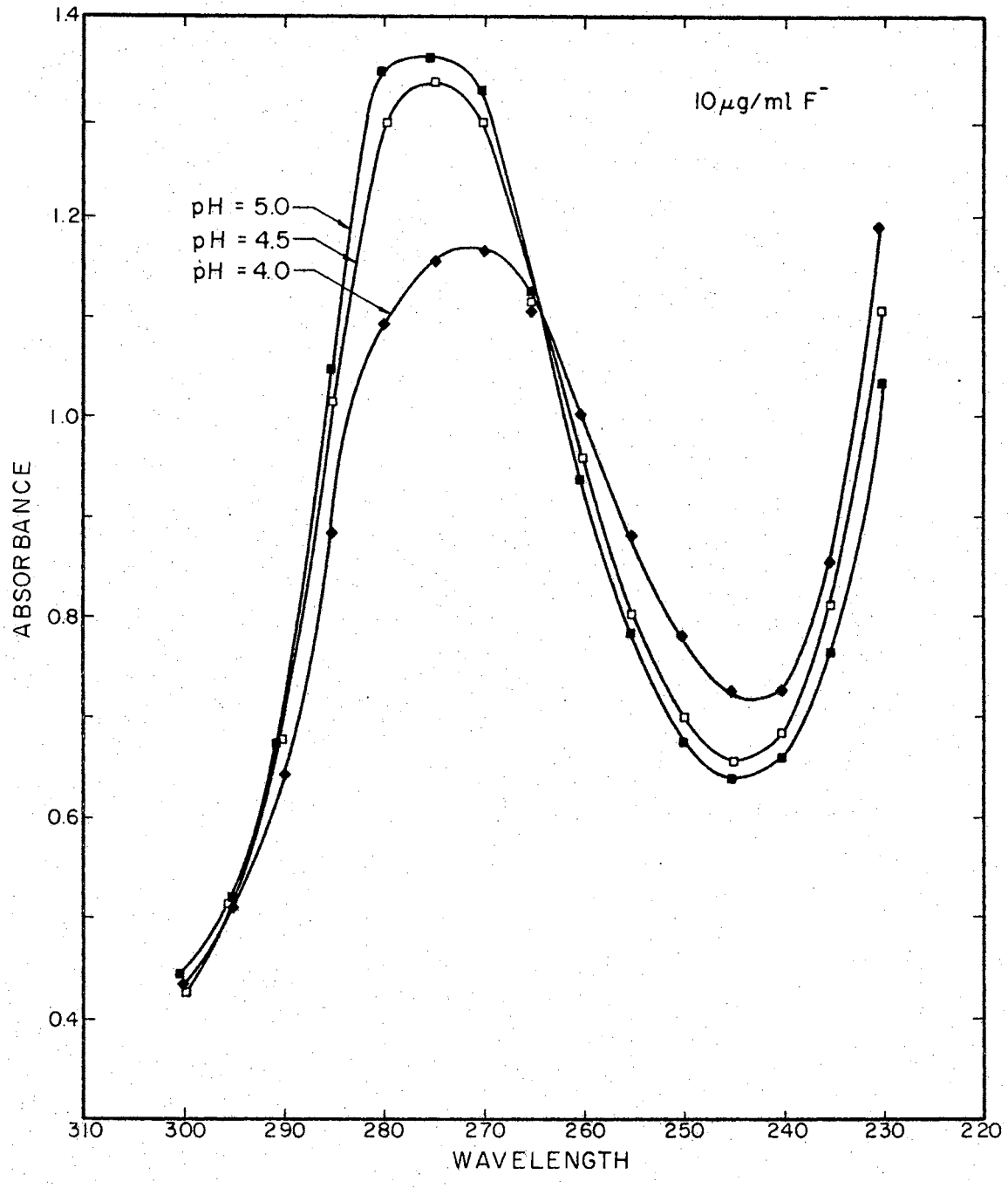


Figure 6. Plot of Absorbance vs. Wavelength for 10 μg/ml F^- in the UV.

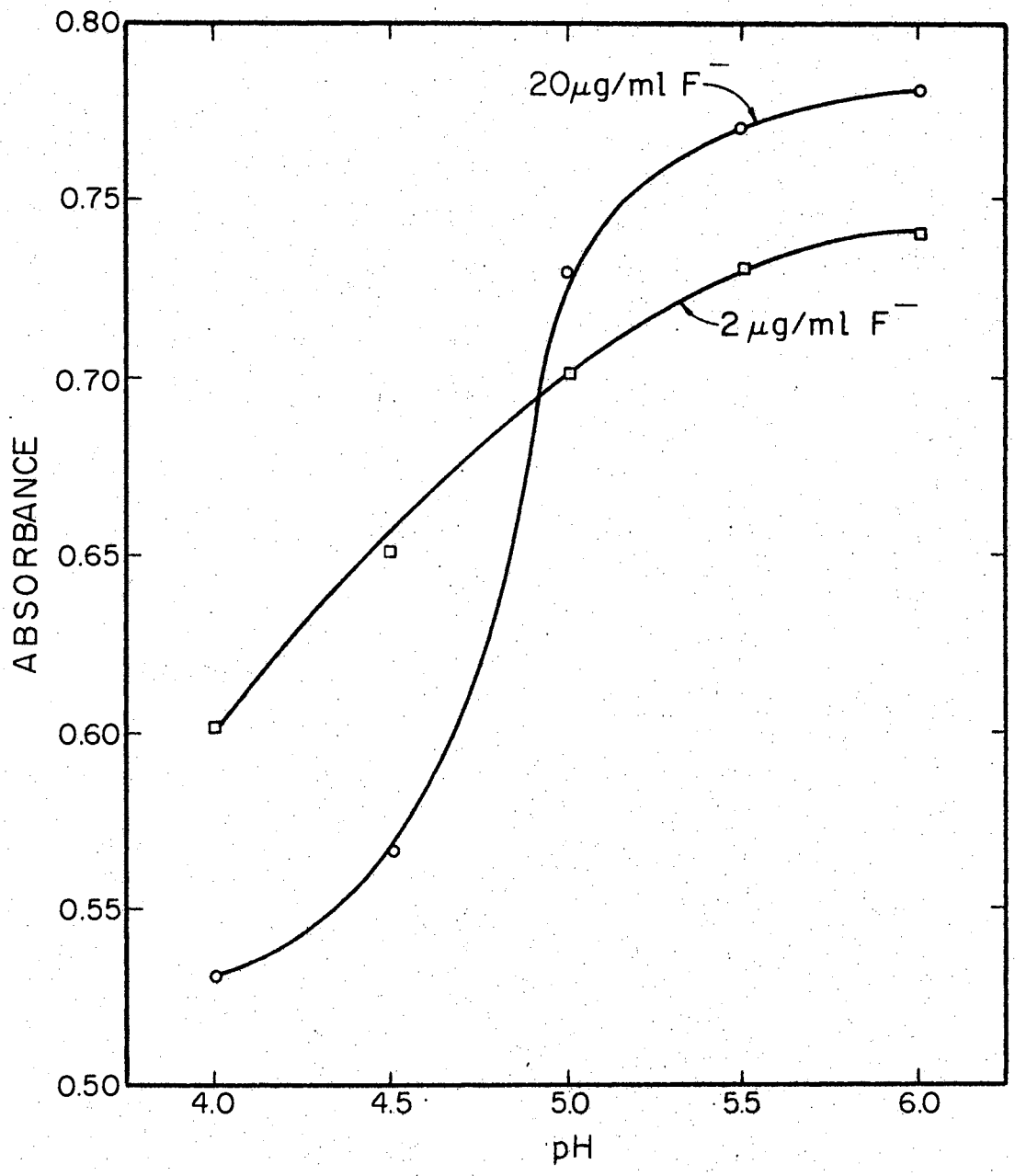


Figure 7. Plot of Absorbance vs. pH in the Visible.

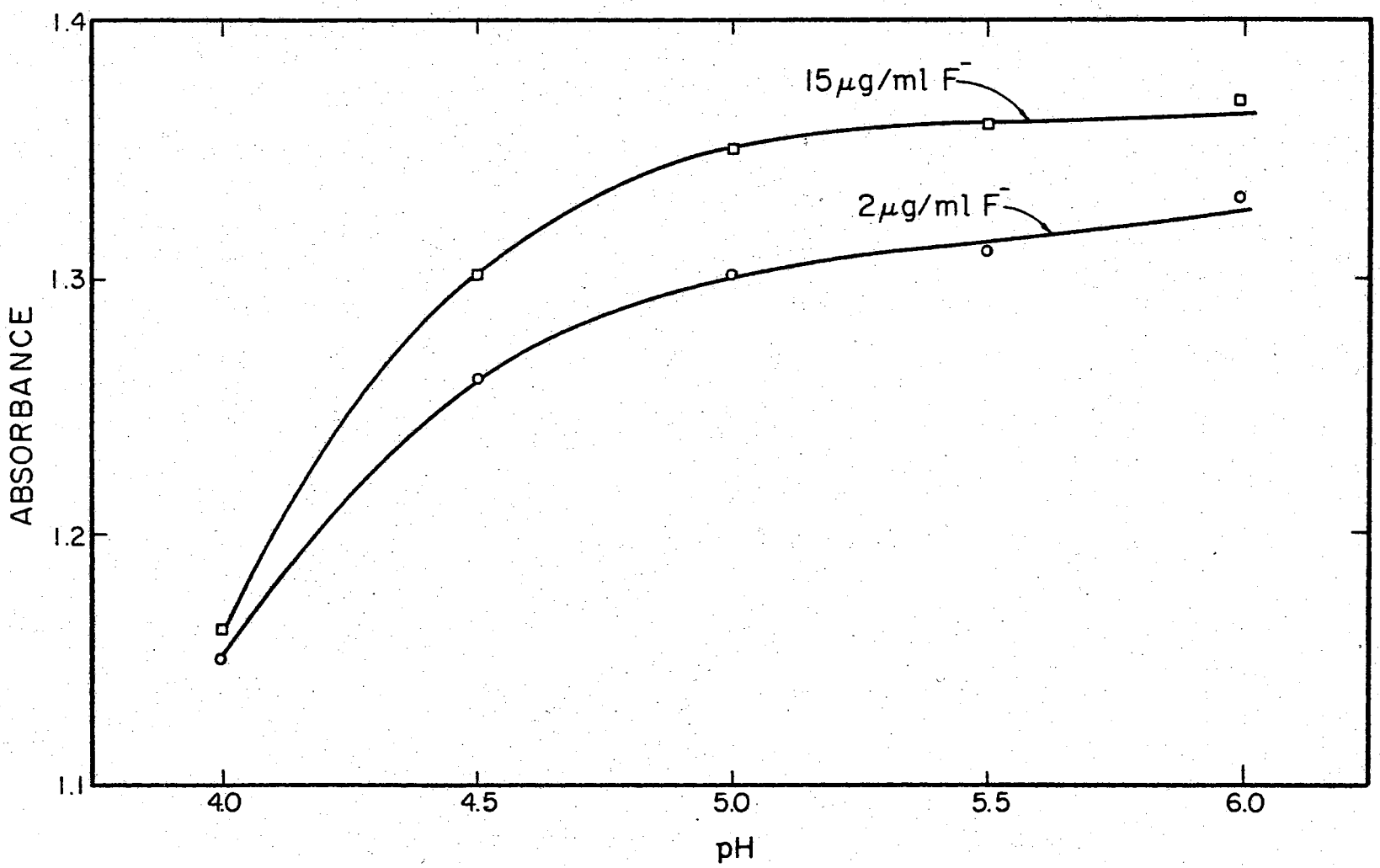


Figure 8. Plot of Absorbance vs. pH in the UV.

pH from 4.5 to 5 gave a sharp rise in absorbance. This could indicate the presence of two forms or two colors of the absorbing species below pH 4.5 and above pH 5. This color change was visible and it changed from wine-red at low pH to blue at higher pH values. The wine red is the color of the reagent and the blue is the color of the ternary fluoride complex.

Ultra Violet Region.--A plot of absorbance at 275 mμ versus pH is given in Fig. 8 for 2 and 15 μg/ml total fluoride ion concentration. A rapid increase of absorbance occurred when the pH was changed from 4 to 4.5. Changing the pH from 5.0 to 6 did not change the absorbance value very much.

Rank of Matrix

Wallace and Katz (8) developed a computer program for the determination of the number of independent absorbing species present in an absorbance matrix. Absorbance data for a series of solutions as a function of wavelength are arranged in a matrix form. This matrix is then subjected to computer analysis for the determination of the rank of matrix and the number of absorbing species.

Both $A_{(ij)}$, the absorbance matrix and $S_{(ij)}$, the error matrix are reduced to form reduced $A_{(ij)}$ and reduced $S_{(ij)}$. From the observation of both reduced matrices, the rank of the system could be determined. Table VI gives $A_{(ij)}$ and $S_{(ij)}$ matrices. Table VII gives the reduced $A_{(ij)}$ and $S_{(ij)}$, the rank of this table is equal to 3. An outline and detailed description of the above method is given by Veatch (9).

A listing of the rank program used in this thesis is given in Appendix A.

Error

Wallace and Katz (8) used an error of ±0.003 absorbance units in their program. Veatch (9) did a study on the error as a function of the rank value. A mean value of ±0.025 absorbance units was used in his work. A loop was added to the original program for the determination of error by Varga and Veatch (12).

The error in absorbance readings was calculated from the following equation (10) derived from Beers law.

$$\frac{\Delta c/c}{\Delta T} = \frac{0.4343}{T \log T}$$

where $\frac{\Delta c}{c}$ = the relative concentration error

T = transmittance

ΔT = photometric error

At a constant photometric error, the relative error is large when the transmittance is very high or very low, and would approach infinity as the transmittance approached 0 or 100% (absorbance approached infinity or 0); a minimum error is attained at a transmittance of about 37% (absorbance = 0.4343). Minimum error at 1% photometric error corresponds to 2.72% relative error.

The value of relative error does not change appreciably from an absorbance of 0.24 to 0.70.

A plot of relative error at constant photometric error versus percent transmittance is given by Ayres (10).

From the above equation, Varga and Veatch (12) derived an equation for the calculation of error in absorbance readings. The derived equation was used in the Rank program for the calculation of $S_{(ij)}$ matrix.

$$S_{(ij)} = .43429 \times \Delta T \times 10^{A_{(ij)}}$$

where ΔT = photometric error

$A_{(ij)}$ = absorbance reading

$S_{(ij)}$ = error in absorbance reading

A study of the value of photometric error to be used was done and the results are given in Table III.

Ten values of ΔT from 0.001 - 0.010 were used. The rank was constant and equal to 2 when the photometric error was varied from 0.004 - 0.010 as shown in the right hand column of Table III.

A value of 0.006 was accepted and used for all the rank evaluation in subsequent work.

The study of the effect of ΔT on the rank value was done on one solution which was 1:1 $Ce^{(III)}$-Alizarin complexone of 0.502×10^{-4} M.

TABLE III

PHOTOMETRIC ERROR SIZE AND RANK OF ABSORBANCE MATRIX

0.0502×10^{-4} M $Ce^{(III)}$-Alizarin Complexone

ΔT Photometric Error	Rank
.001	3
.002	3
.003	3
.004	2
.005	2
.006	2*
.007	2
.008	2
.009	2
.010	2

*Accepted value

Three Dimensional Plotting Program

A listing of the plotting program used is given in Appendix B. Plotting the spectrophotometric data in three dimensions was helpful in studying absorbance matrices. Using the rank program the number of absorbing species could be determined. By the help of the three dimension plots, species were identified by observing the peaks and valleys and where they occur.

Each absorbance matrix was plotted separately. Wavelength in millimicrons, solutions of different pH value with constant fluoride ion concentration and absorbance on the y, x and z axes.

The curves in those plots represented the points of equal absorbance values (isoabsorbance lines) resembling the contours on a topographical map. A shaded area in those plots represented a valley.

Three Dimensional Plots in the Visible

1. 1.0×10^{-4} M $Ce^{(III)}$-Alizarin Complexone: The contour map is given in Fig. 9 and the absorbance matrix is given in Table VI.

   Maximum absorbance increased as pH increased, the highest value was at pH 5 and 540 mμ. A ridge was observed at 480 mμ.

2. 2 μg/ml Total Fluoride Ion Concentration: The contour map is given in Fig. 10 and the absorbance matrix is given in Table VIII. The rank of this matrix is 2.

   Maximum absorbance increased as the pH was increased. A peak was at pH 5.5 - 6 and a wavelength of 560 mμ. A ridge was at about 500 mμ.

3. 5 μg/ml Total Fluoride Ion Concentration: The contour map is

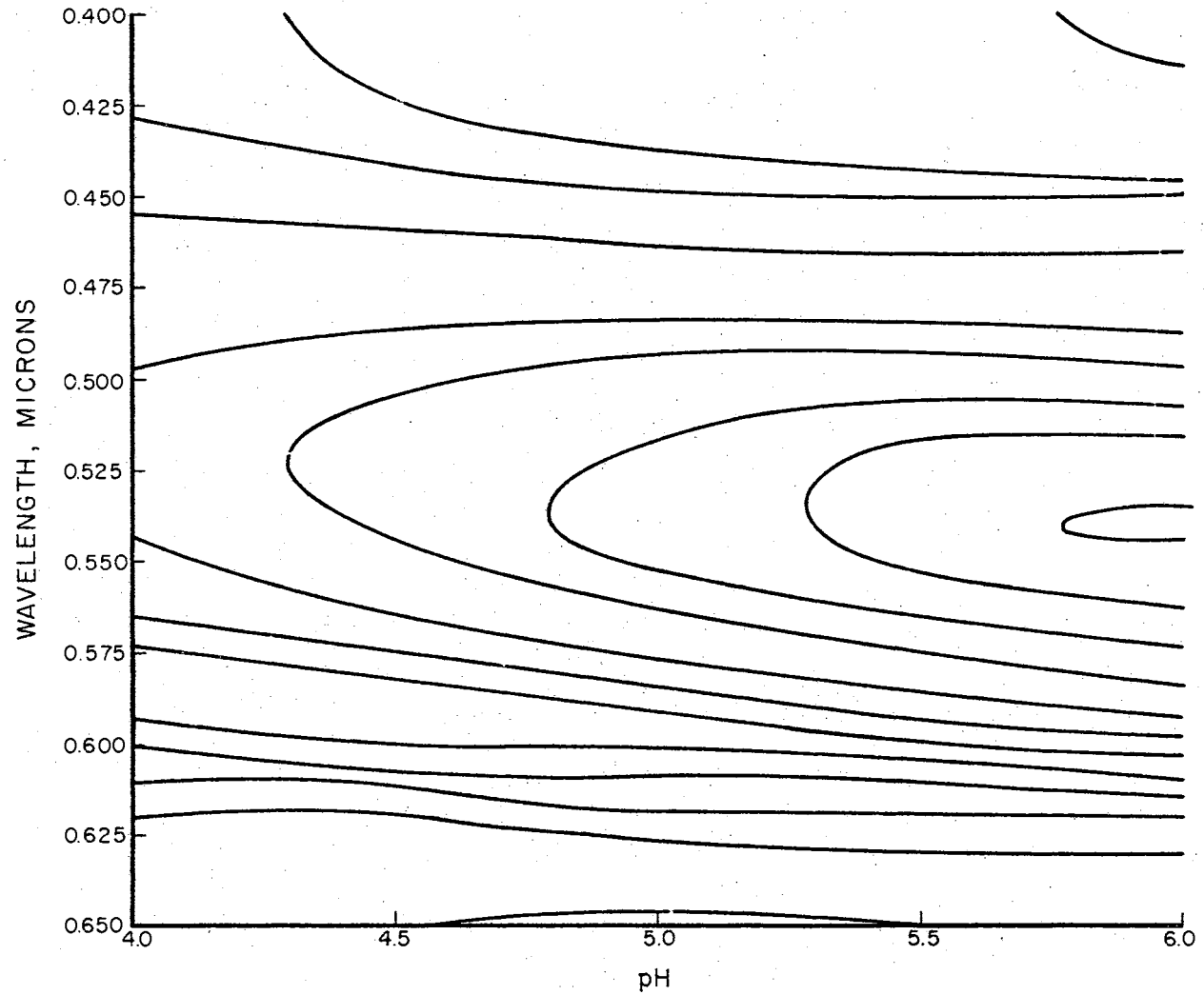


Figure 9. Contour Map of the 1.00×10^{-4} M $Ce^{(III)}$-Alizarin Complexone Absorbance of Table VI in the Visible.

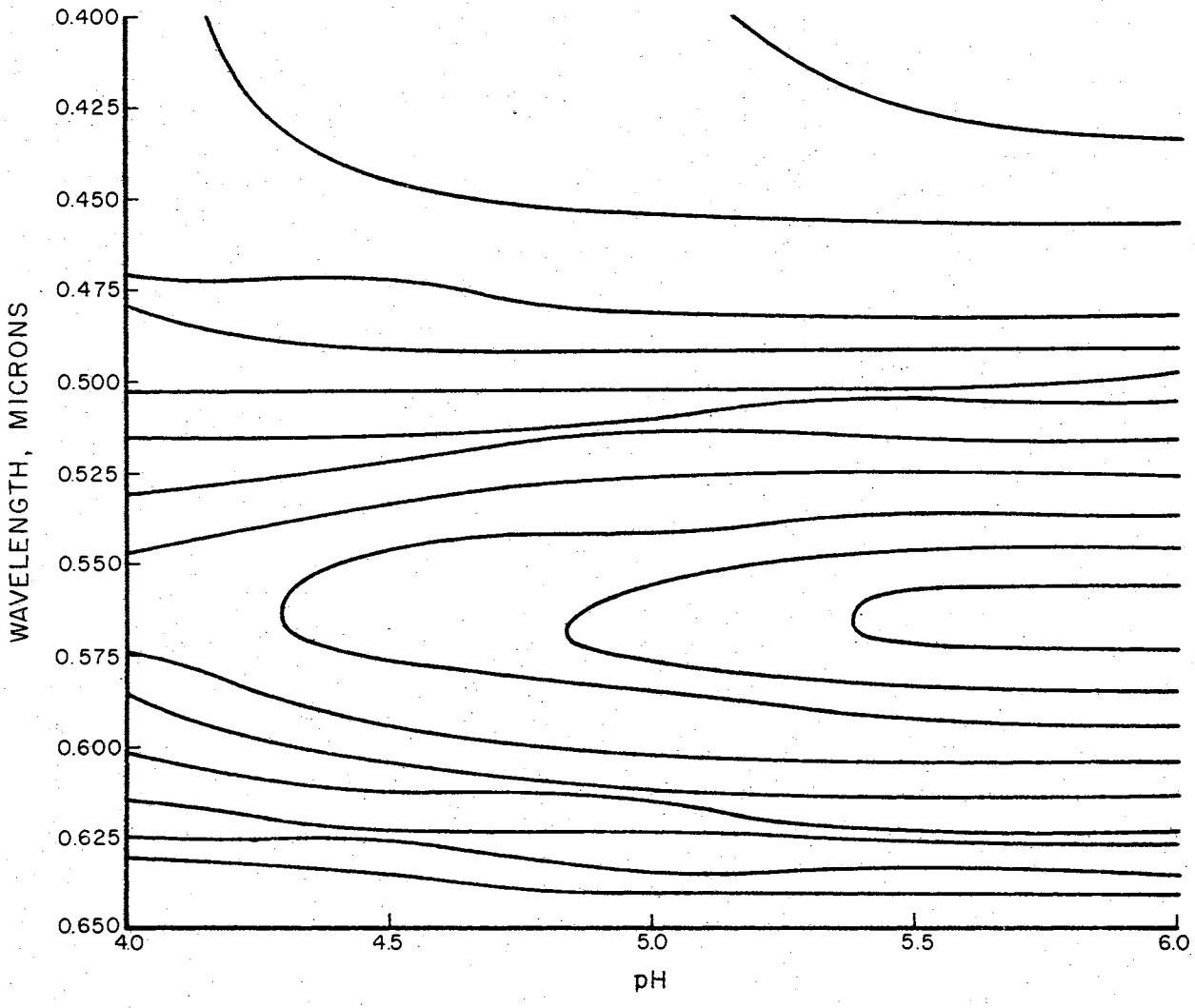


Figure 10. Contour Map of 2 µg/ml F^- Absorbance of Table VIII in the Visible.

given in Fig. 11; the absorbance matrix is in Table IX.

The rank of matrix is 2. The peak now extends to be from pH 5.0 - 6.0. Wavelengths of maximum absorbance did not change by changing the fluoride ion concentration.

4. 10 μg/ml Total Fluoride Ion Concentration: The contour map is given in Fig. 12; the absorbance matrix is in Table X.

The rank of matrix is 2. The peak here was on the pH value of 6 and on the same wavelength.

5. 15 μg/ml Total Fluoride Ion Concentration: The contour map is in Fig. 13; the absorbance matrix is in Table XI.

The rank of matrix is equal to 2. This plot was similar to Fig. 12; only the whole peak was shifted toward a higher pH.

Three Dimensional Plots in the Ultra Violet

1. 0.502×10^{-4} M $Ce^{(III)}$-Alizarin Complexone: The contour map is given in Fig. 14; the absorbance matrix is in Table XIII. Rank of matrix is 2.

In this plot two peaks at 265 mμ and a valley at 245 mμ were observed. The first peak was at pH 4.5, the second was at pH 6.0 and a valley extended from pH 5.0 - 6.0.

2. 2 μg/ml Total Fluoride Ion Concentration: The contour map is in Fig. 15 and the absorbance matrix is in Table XIV. The rank of this matrix is equal to 2.

A peak at about 275 mμ and a valley at about 240 mμ were observed. Maximum absorbance increased as the pH was increased, the highest value was at pH 6.

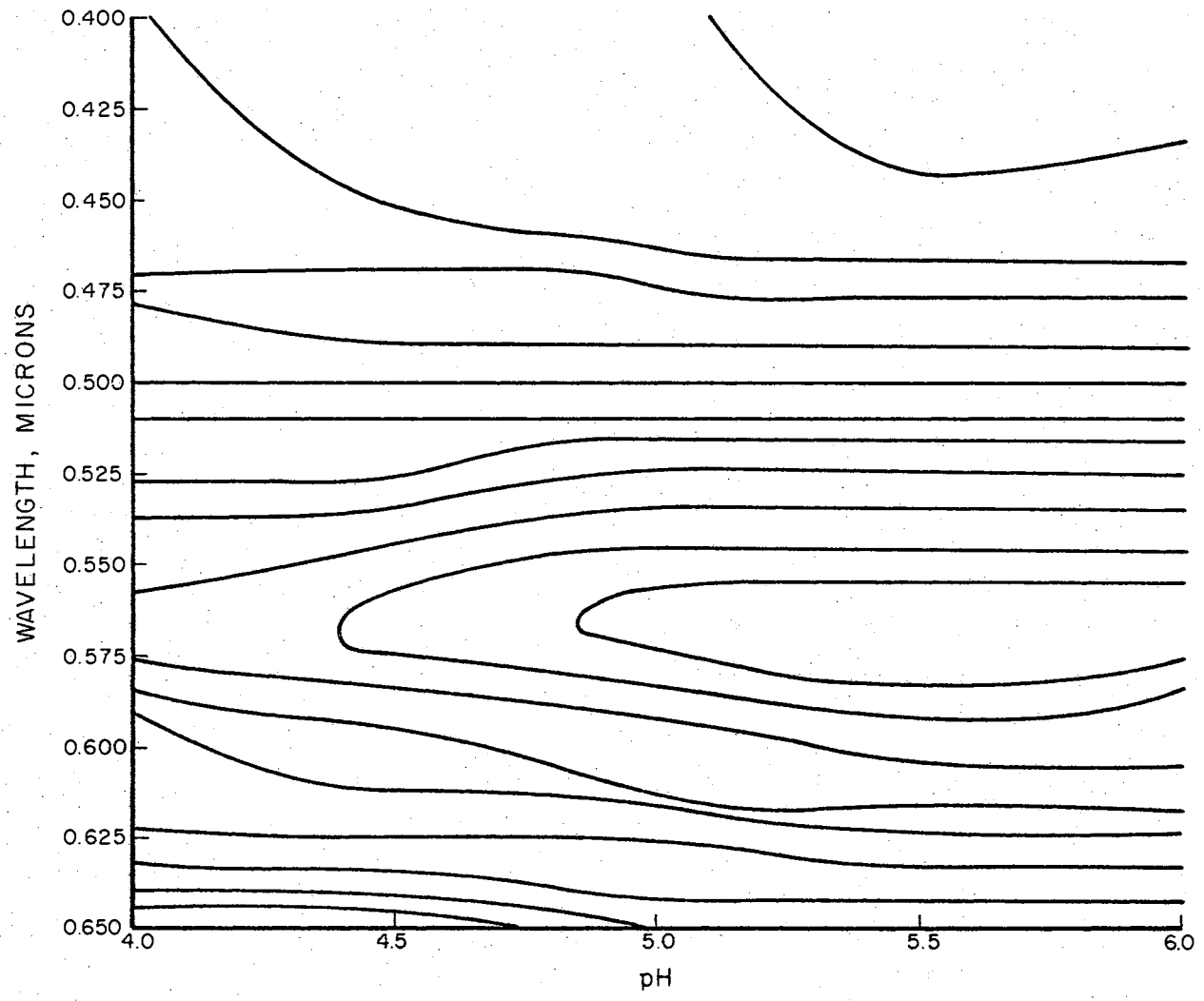


Figure 11. Contour Map of 5 μg/ml F^- Absorbance of Table IX in the Visible.

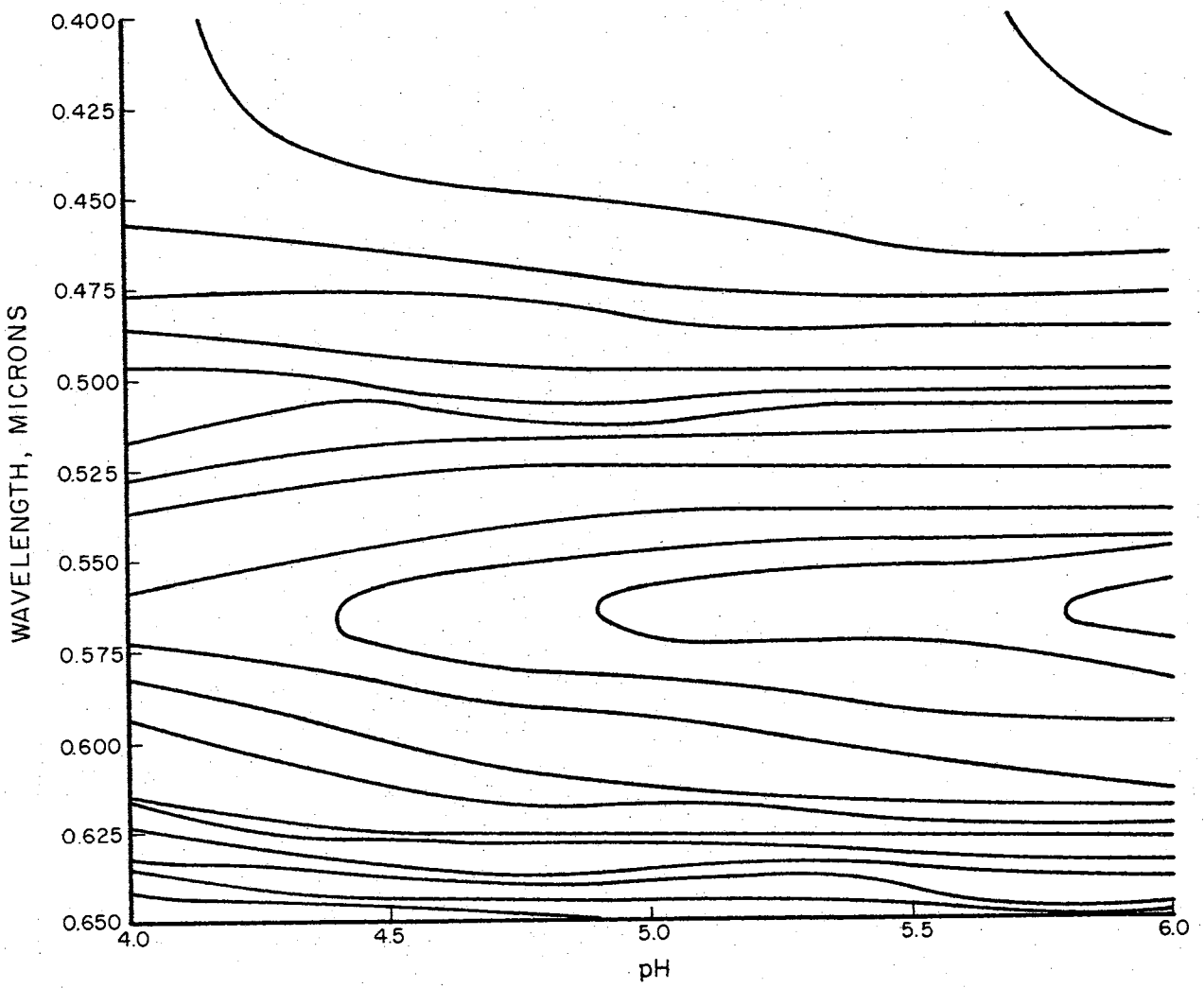


Figure 12. Contour Map of 10 µg/ml F^- Absorbance of Table X in the Visible.

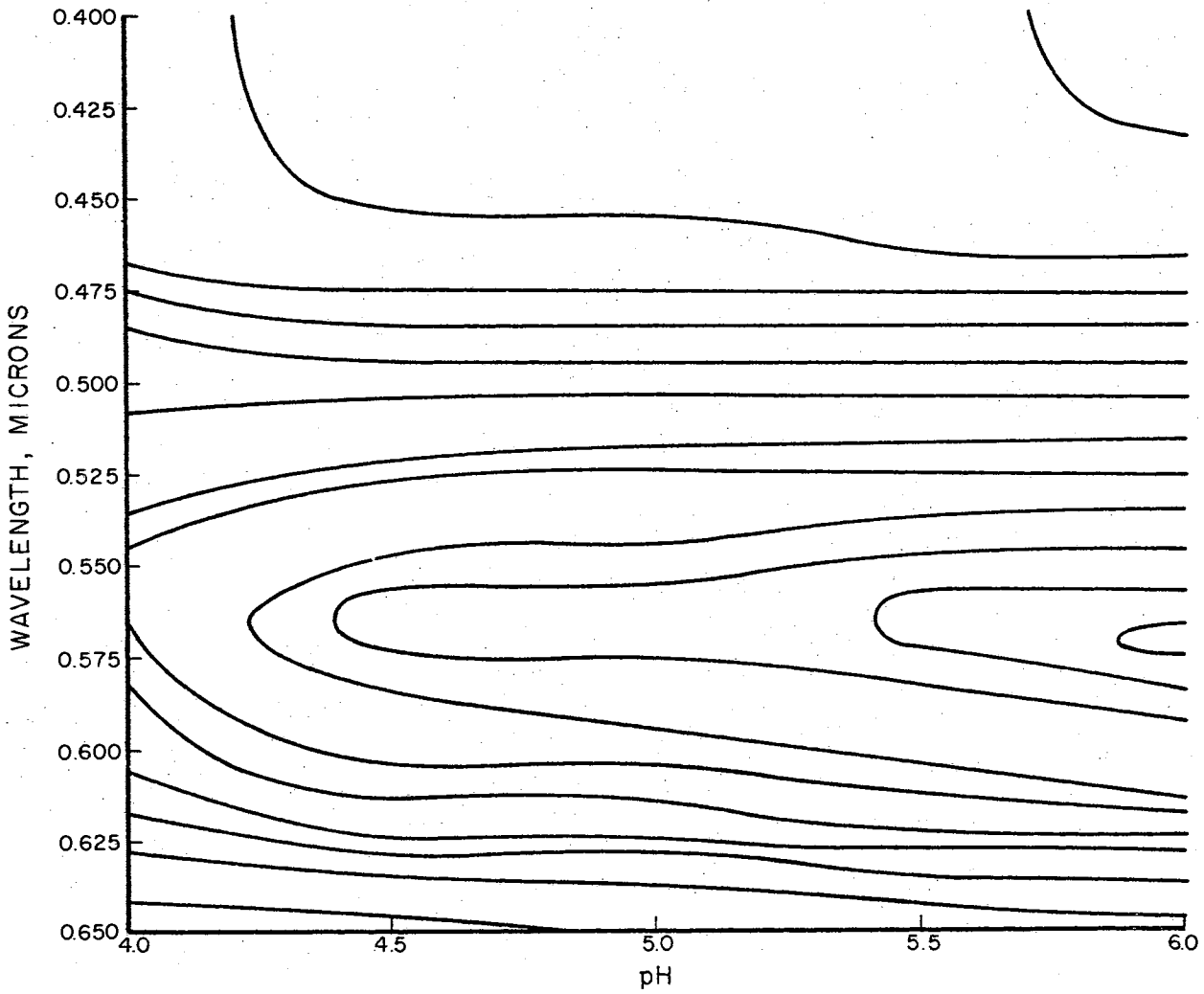


Figure 13. Contour Map of 15 µg/ml F^- Absorbance of Table XI in the Visible.

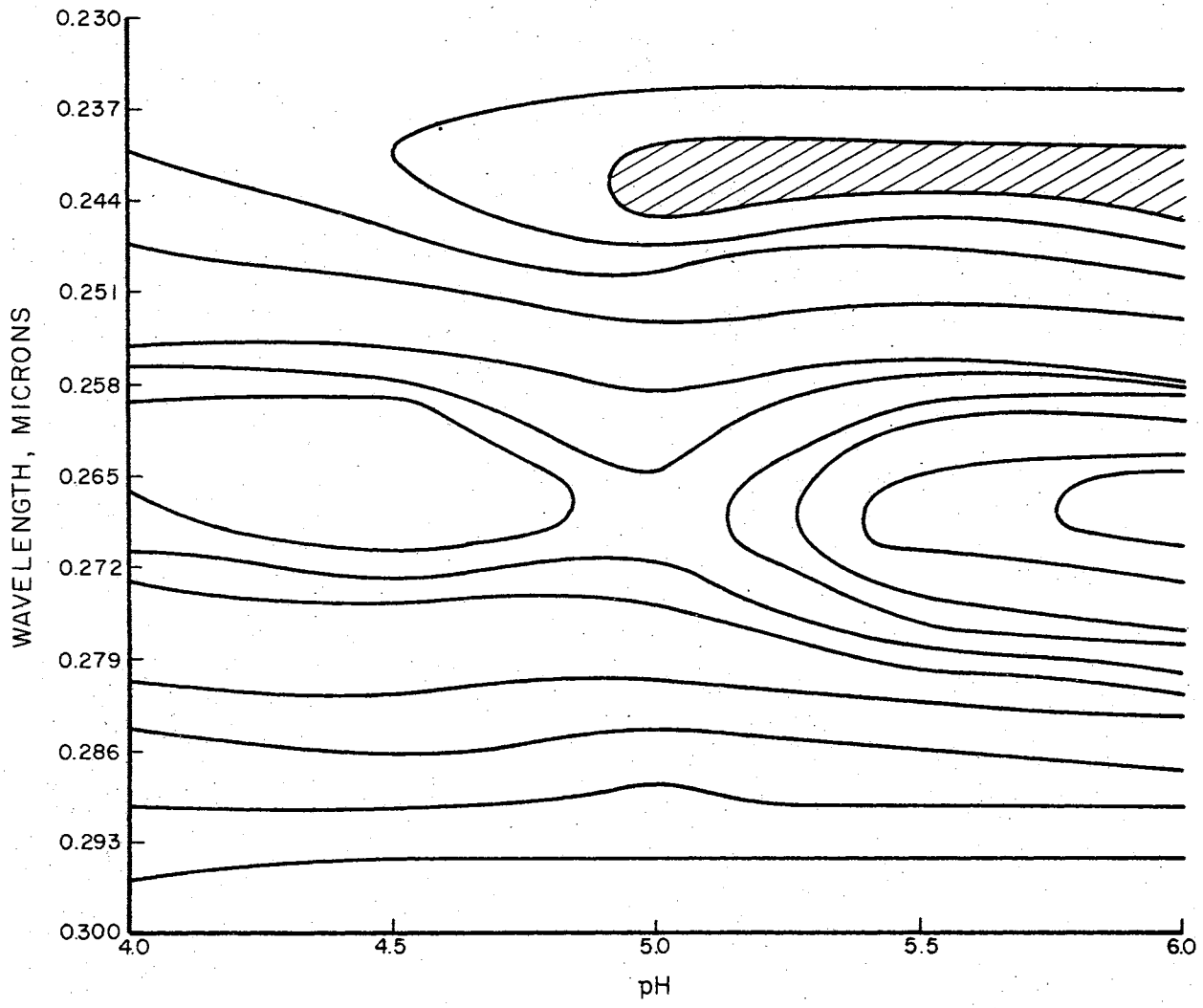


Figure 14. Contour Map of 0.502×10^{-4} M $Ce^{(III)}$-Alizarin Complexone Absorbance of Table XIII in the UV.

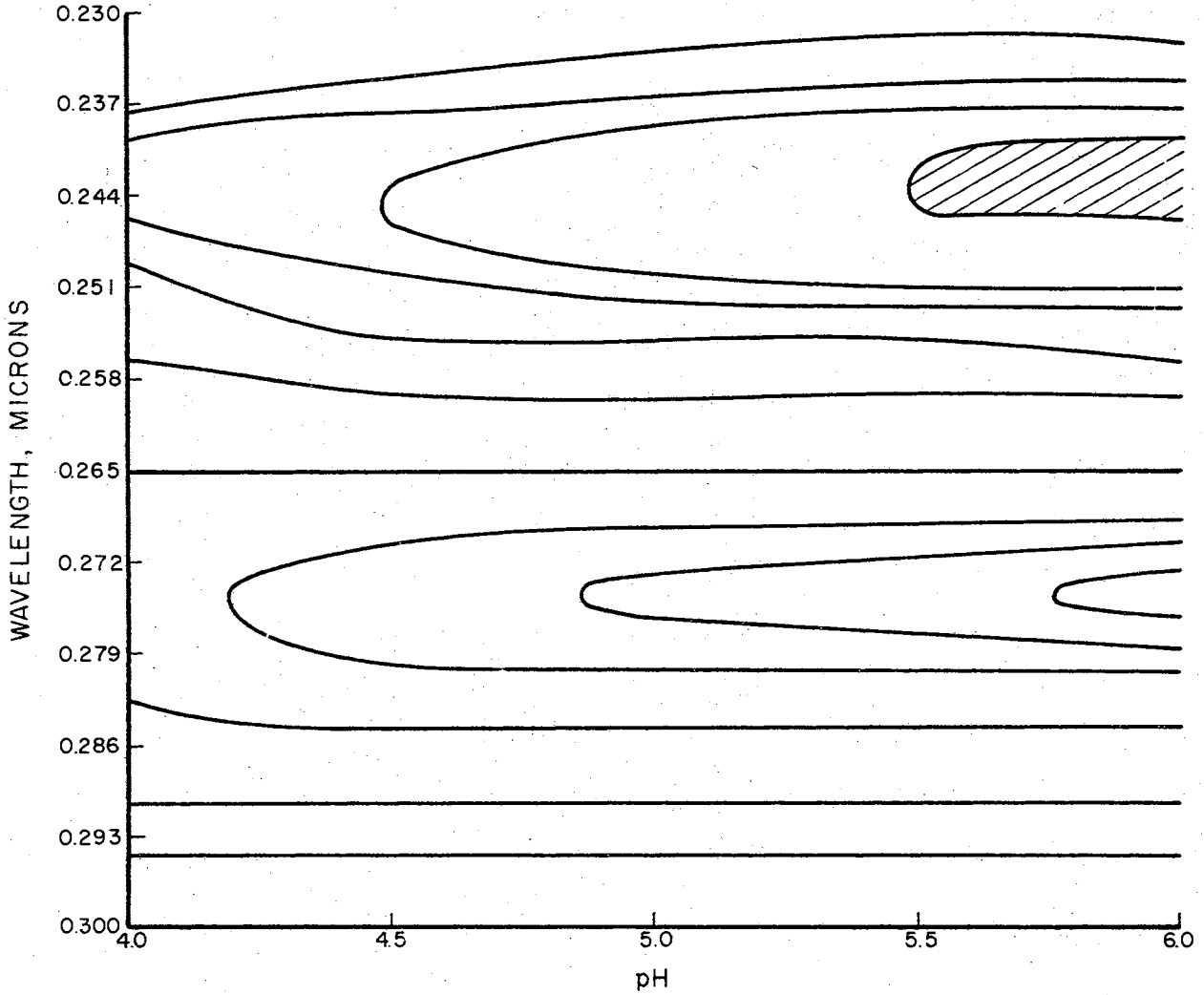


Figure 15. Contour Map of 2 µg/ml F^- Absorbance of Table XIV in the UV.

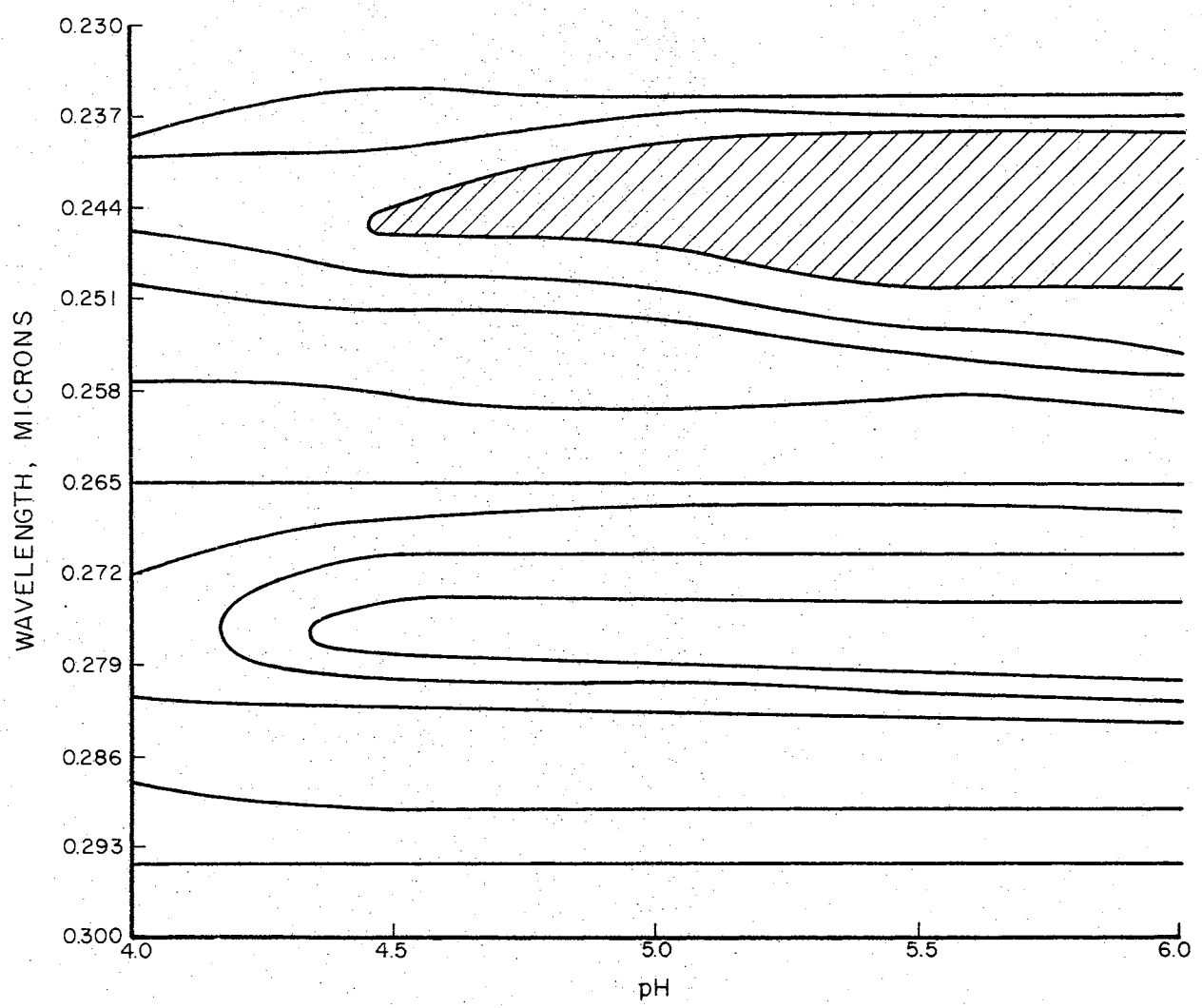


Figure 16. Contour Map of 5 μg/ml F^- Absorbance of Table XV in the UV.

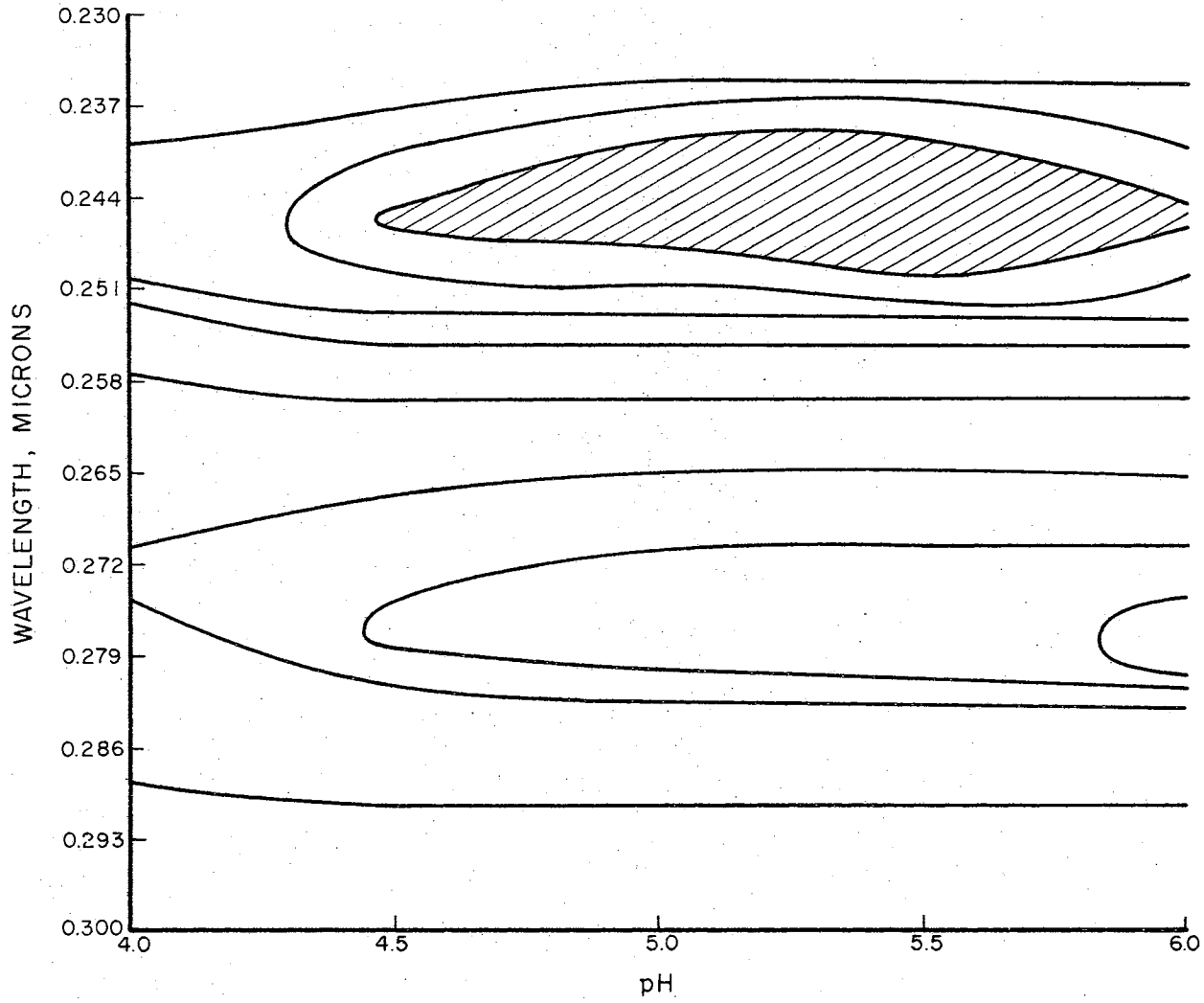


Figure 17. Contour Map of 10 µg/ml F^- Absorbance of Table XVI in the UV.

3. 5 μg/ml Total Fluoride Ion Concentration: The contour map is in Fig. 16; the absorbance matrix is in Table XV. The rank of matrix is equal to 2.

Maximum absorbance was at the same wavelength as in Fig. 15, but the peak here was of the same height from pH 4.5 - 6.

4. 10 μg/ml Total Fluoride Ion Concentration: The contour map is given in Fig. 17; the absorbance matrix is in Table XVI. Rank of matrix equals to 2.

Maximum absorbance increased as the pH was increased. The highest value was at pH = 6. The valley was of the same depth from pH 4.5 - 6 and a ridge at about 250 mμ.

Calculation of Free Fluoride Ion Concentration at Maximum Absorbance.--For all the solutions prepared, calculations of free fluoride ion at the wavelength of maximum absorbance and at all the pH values studied was done by using equations (1), (2), and (3). Ternary fluoride complex is abbreviated as Ce-AC-F.

$$HF \rightleftarrows H^+ + F^-$$

$$Ka = \frac{[H^+]\,[F^-]}{[HF]} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$C_{F^-} = [HF] + [F^-] + [Ce\text{-}AC\text{-}F] \quad \ldots\ldots\ldots \quad (2)$$

$$[Ce - Ac - F] = \frac{A}{\epsilon} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$C_{F^-} = [HF] + [F^-] + \frac{A}{\epsilon}$$

$$= \frac{[H^+]\,[F^-]}{Ka} + [F^-] + \frac{A}{\epsilon}$$

$$[F^-] = \frac{C_F - \frac{A}{\epsilon}}{\frac{[H^+]}{Ka} + 1}$$

where C_{F^-} = total fluoride ion concentration

K_a = $10^{-3.62}$ (given in reference 11)

ϵ_{570} = molar absorptivity of Ce - Ac - F at 570 mμ

ϵ_{275} = molar absorptivity of Ce - Ac - F at 275 mμ

$[H^+]$ = measured with pH meter

A = absorbance value at a certain pH and total fluoride ion concentration.

Calculation of Molar Absorptivity: The molar absorptivity at the wavelength of maximum absorption, 570 mμ in the visible and 275 mμ in the ultra violet regions was done by assuming that at high fluoride ion concentration all the $Ce^{(III)}$-Alizarin complexone was in the form of the ternary fluoride complex.

The absorbance value at 570 mμ for the 20 μg/ml F^- in the visible region, and the absorbance value at 275 mμ for 15 μg/ml F^- in the ultra-violet, both solutions at pH = 6 were used in the calculation of molar absorptivity using the equations below:

$$\epsilon = \frac{A}{[Ce\text{-}AC\text{-}F]}$$

$$\epsilon_{570} = \frac{0.800}{1.00 \times 10^{-4}} = 8 \times 10^3$$ Molar absorptivity in the visible at 570 mμ.

$$\epsilon_{275} = \frac{1.37}{0.502 \times 10^{-4}} = 2.73 \times 10^4$$ Molar absorptivity in the ultra-violet at 275 mμ.

The results of the calculations of free fluoride ion are given in Table IV and Table V. By looking at the value of the free fluoride in Table IV, it can be seen that when the molar ratio of (F^-):$(Ce^{III}$-Alizarin complexone) was less than 1:1, the free fluoride concentration decreased on the pH values was increased. Meaning that at higher pH,

more of the ternary fluoride complex is being formed. When the molar ratio of (F^-):$(Ce^{(III)}$-Alizarin complexone) was more than 1:1, increasing the pH value gave a higher fluoride ion concentration in solution according to the reaction:

$$HF \rightleftarrows H^+ + F^-$$

When the $[H^+]$ is decreased or the pH is increased, more of the HF will dissociate to give a higher concentration of fluoride ion in solution.

The above calculation shows that the fluoride ion reacts with the reagent in a 1:1 ratio, this agrees with what has been found by Leonard and West (3) using the Job's plot of continuous variation.

TABLE IV

MOLARITY X 10^{-4} FREE FLUORIDE ION CONCENTRATION AT 570 mμ

1.00×10^{-4} M $Ce^{(III)}$-ALIZARIN COMPLEXONS

	Molarity x 10^{-4} Total Fluoride Ion Concentration				
pH	1.052	2.630	5.26	7.89	10.52
4.0	0.229	1.30	3.159	5.078	6.975
4.5	0.199	1.518	3.762	6.018	8.310
5.0	0.176	1.641	4.173	6.723	9.197
5.5	0.138	1.642	4.238	6.827	9.380
6.0	0.126	1.683	4.256	6.877	9.482

TABLE V

MOLARITY X 10^{-4} FREE FLUORIDE ION CONCENTRATION AT 275 mμ

0.502×10^{-4} M $Ce^{(III)}$-ALIZARIN COMPLEXONE

	Molarity x 10^{-4} Total Fluoride Ion Concentration			
pH	1.052	2.630	5.26	7.89
4.0	0.446	1.555	3.414	5.272
4.5	0.506	1.838	4.091	6.358
5.0	0.553	2.052	4.570	7.098
5.5	0.562	2.100	4.690	7.268
6.0	0.563	2.119	4.728	7.358

CHAPTER IV

INTERPRETATION OF RESULTS

Summary and Conclusion

The number of absorbing species present in the solutions that contain fluoride was determined by the rank program and was equal to two. Those species were identified as the reagent $Ce^{(III)}$-Alizarin complexone and the ternary fluoride complex.

In both the visible and the ultra-violet regions, it was observed from the contour plots that as the pH value was increased, maximum absorbance increased; also when the concentration of fluoride ion was increased, higher pH values have the highest maximum absorbance. This could be explained by using the following two equations:

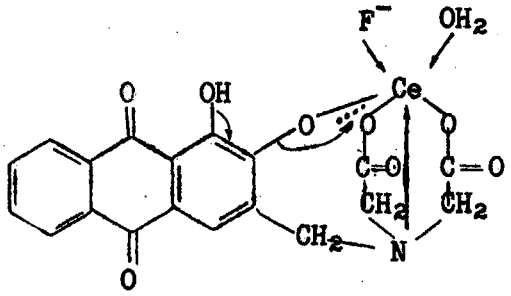
$$HF \rightleftharpoons H^+ + F^-$$

$$Ce - AC + F^- \rightleftharpoons H^+ + [Ce - AC - F]^{-2}$$

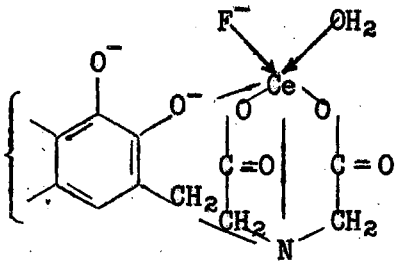
Looking at both equations it is obvious that when the pH increases (decreasing $[H^+]$), both equilibria will shift to the right leading to a higher fluoride ion concentration in the first equation, and higher concentration of the ternary fluoride complex in the second equation. But when the fluoride ion concentration increases, the direction of reaction in the first equation will be to the left while in the second equation it will be to the right. From the experimental results,

increasing the fluoride ion concentration in the permissible range, gave an increase in maximum absorbance. Therefore, the second equation is the one that explains the system more closely.

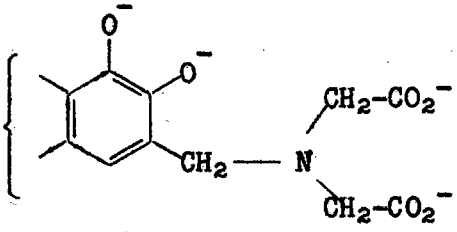
Actually the formation of the ternary fluoride complex does not include a displacement of hydrogen by a fluoride ion, but it is due to the strong electrophilic properties of the fluoride atom (3). From the structural formula of the ternary fluoride complex, we can see that a partial double bond could be formed between the oxygen and the metal. Electrons will be attracted from the 1-hydroxyl group, and this will help the deprotonation of this hydroxyl group.



The structure of the resulting compound will be similar to that of the free Alizarin complexone at pH ≥ 13, that is the I^{-4} form which is also blue.



Ternary Fluoride Complex



I^{-4} at pH ≥ 13

TABLE VI

ABSORBANCE MATRIX FOR $Ce^{(III)}$-ALIZARIN COMPLEXONE AND S ERROR MATRIX IN THE VISIBLE

λ	pH 4.0	4.5	5.0	5.5	6.0
650	0.07500000	0.06000000	0.02300000	0.06500000	0.06800000
640	0.08400000	0.08600000	0.08900000	0.09500000	0.10200000
630	0.11300000	0.11700000	0.12400000	0.13700000	0.15000000
620	0.15400000	0.16700000	0.18000000	0.20000000	0.21100000
610	0.20000000	0.22100000	0.24600000	0.27400000	0.29500000
600	0.24500000	0.27600000	0.30700000	0.34500000	0.37000000
590	0.28400000	0.32300000	0.36000000	0.40000000	0.43000000
580	0.32000000	0.36400000	0.40800000	0.45200000	0.48500000
570	0.35400000	0.40200000	0.45200000	0.50400000	0.54300000
560	0.38800000	0.44500000	0.49000000	0.55000000	0.59000000
550	0.42000000	0.46100000	0.53000000	0.59000000	0.62000000
540	0.43600000	0.49000000	0.54800000	0.60000000	0.63000000
530	0.44500000	0.49600000	0.54800000	0.59800000	0.62000000
520	0.45000000	0.49600000	0.53800000	0.57800000	0.60000000
510	0.44900000	0.48800000	0.52000000	0.55000000	0.56200000
500	0.44500000	0.47000000	0.49000000	0.50800000	0.52000000
490	0.42300000	0.44100000	0.45000000	0.45800000	0.46000000
480	0.39600000	0.41000000	0.40900000	0.40600000	0.40300000
470	0.36600000	0.36600000	0.35600000	0.35000000	0.34500000
460	0.33500000	0.32800000	0.31200000	0.30000000	0.29500000
450	0.30500000	0.29000000	0.27200000	0.25700000	0.25000000
440	0.28000000	0.26000000	0.24100000	0.22500000	0.22000000
430	0.26000000	0.23700000	0.22000000	0.20500000	0.19800000
420	0.24500000	0.22300000	0.20400000	0.19000000	0.18300000
410	0.23500000	0.20800000	0.19200000	0.17800000	0.17200000
400	0.22700000	0.20400000	0.18700000	0.17500000	0.17000000

ORIGINAL S MATRIX

0.00309693	0.00299179	0.00274746	0.00302643	0.00304741
0.00316178	0.00317637	0.00319839	0.00324288	0.00329557
0.00338011	0.00341139	0.00346682	0.00357216	0.00368071
0.00371476	0.00382764	0.00394395	0.00412982	0.00423576
0.00412982	0.00433442	0.00459125	0.00489701	0.00513962
0.00458069	0.00491941	0.00528361	0.00576675	0.00610845
0.00501108	0.00548190	0.00596941	0.00654532	0.00701344
0.00544416	0.00602464	0.00666701	0.00737787	0.00796033
0.00588750	0.00657553	0.00737787	0.00831632	0.00909769
0.00636694	0.00725991	0.00805251	0.00924551	0.01013750
0.00685379	0.00753236	0.00882940	0.01013750	0.01086253
0.00711101	0.00805251	0.00920303	0.01037364	0.01111555
0.00725991	0.00816453	0.00920303	0.01032597	0.01086253
0.00734397	0.00816453	0.00899355	0.00986123	0.01037364
0.00732708	0.00801561	0.00862942	0.00924551	0.00950454
0.00725991	0.00769008	0.00805251	0.00839327	0.00862842
0.00690130	0.00719335	0.00734397	0.00748051	0.00751504
0.00648532	0.00669778	0.00666701	0.00663538	0.00659069
0.00605245	0.00605245	0.00591468	0.00583353	0.00576675
0.00563548	0.00554538	0.00534480	0.00519913	0.00513962
0.00525934	0.00508079	0.00487451	0.00470903	0.00463373
0.00496514	0.00474167	0.00453870	0.00437453	0.00432445
0.00474167	0.00449708	0.00432445	0.00417764	0.00411084
0.00458069	0.00435443	0.00416803	0.00403581	0.00397129
0.00447642	0.00420660	0.00405444	0.00392583	0.00387196
0.00439472	0.00416803	0.00400803	0.00389880	0.00385417

TABLE VII

REDUCED ABSORBANCE AND S ERROR MATRIX FOR $Ce^{(III)}$-ALIZARIN COMPLEXONE IN THE VISIBLE

λ \ pH	4.0	4.5	5.0	5.5	6.0
650	0.63000000	0.43600000	0.54800000	0.49000000	0.60000000
640	0.00000000	0.13198413	0.05453969	0.09555556	0.01890476
630	0.00000000	0.00000000	-0.04769470	-0.01311702	-0.00376385
620	0.00000000	0.00000000	0.00000000	-0.01312254	0.00126227
610	0.00000000	0.00000000	0.00000000	0.00000000	-0.00594318
600	0.00000000	0.00000000	0.00000000	0.00000000	-0.00507661
590	0.00000000	0.00000000	0.00000000	0.00000000	-0.00684534
580	0.00000000	0.00000000	0.00000000	0.00000000	-0.00706459
570	0.00000000	0.00000000	0.00000000	0.00000000	-0.00926733
560	0.00000000	0.00000000	0.00000000	0.00000000	-0.00735504
550	0.00000000	0.00000000	0.00000000	0.00000000	-0.00165223
540	0.00000000	0.00000000	0.00000000	0.00000000	-0.00669895
530	0.00000000	0.00000000	0.00000000	0.00000000	0.00523665
520	0.00000000	0.00000000	0.00000000	0.00000000	0.00181068
510	0.00000000	0.00000000	0.00000000	0.00000000	0.00620447
500	0.00000000	0.00000000	0.00000000	0.00000000	0.00068220
490	0.00000000	0.00000000	0.00000000	0.00000000	0.00493386
480	0.00000000	0.00000000	0.00000000	0.00000000	0.00559550
470	0.00000000	0.00000000	0.00000000	0.00000000	0.00338672
460	0.00000000	0.00000000	0.00000000	0.00000000	0.00053464
450	0.00000000	0.00000000	0.00000000	0.00000000	-0.00380138
440	0.00000000	0.00000000	0.00000000	0.00000000	-0.00283537
430	0.00000000	0.00000000	0.00000000	0.00000000	-0.00144459
420	0.00000000	0.00000000	0.00000000	0.00000000	-0.00129006
410	0.00000000	0.00000000	0.00000000	0.00000000	-0.00277328
400	0.00000000	0.00000000	0.00000000	0.00000000	-0.00263981

REDUCED S MATRIX

0.01111555	0.00711101	0.00920303	0.00805251	0.01037364
0.00000000	0.00743141	0.00825015	0.00779641	0.00873175
0.00000000	0.00000000	0.00476857	0.00531459	0.00489118
0.00000000	0.00000000	0.00000000	0.02006320	0.02073386
0.00000000	0.00000000	0.00000000	0.00000000	0.01105133
0.00000000	0.00000000	0.00000000	0.00000000	0.01226889
0.00000000	0.00000000	0.00000000	0.00000000	0.01405470
0.00000000	0.00000000	0.00000000	0.00000000	0.01581133
0.00000000	0.00000000	0.00000000	0.00000000	0.01799687
0.00000000	0.00000000	0.00000000	0.00000000	0.02109725
0.00000000	0.00000000	0.00000000	0.00000000	0.00793395
0.00000000	0.00000000	0.00000000	0.00000000	0.00841979
0.00000000	0.00000000	0.00000000	0.00000000	0.02110133
0.00000000	0.00000000	0.00000000	0.00000000	0.02107053
0.00000000	0.00000000	0.00000000	0.00000000	0.02118399
0.00000000	0.00000000	0.00000000	0.00000000	0.01883277
0.00000000	0.00000000	0.00000000	0.00000000	0.01898744
0.00000000	0.00000000	0.00000000	0.00000000	0.02140846
0.00000000	0.00000000	0.00000000	0.00000000	0.01616720
0.00000000	0.00000000	0.00000000	0.00000000	0.01448726
0.00000000	0.00000000	0.00000000	0.00000000	0.00587021
0.00000000	0.00000000	0.00000000	0.00000000	0.01255597
0.00000000	0.00000000	0.00000000	0.00000000	0.01388156
0.00000000	0.00000000	0.00000000	0.00000000	0.01234985
0.00000000	0.00000000	0.00000000	0.00000000	0.01667229
0.00000000	0.00000000	0.00000000	0.00000000	0.01353303

TABLE VIII

ABSORBANCE MATRIX OF 2 μg/ml F^- AND S ERROR MATRIX IN THE VISIBLE

pH / λ	4.0	4.5	5.0	5.5	6.0
650	0.17100000	0.19600000	0.20800000	0.22300000	0.22500000
640	0.23100000	0.27000000	0.29000000	0.30300000	0.31200000
630	0.30000000	0.35400000	0.37900000	0.39500000	0.40000000
620	0.37600000	0.44200000	0.46800000	0.48800000	0.49800000
610	0.43800000	0.50500000	0.54400000	0.56000000	0.57000000
600	0.48000000	0.55000000	0.58000000	0.60400000	0.61200000
590	0.51000000	0.58200000	0.61200000	0.63900000	0.65000000
580	0.55000000	0.62000000	0.66000000	0.69000000	0.69800000
570	0.58500000	0.65800000	0.69500000	0.73000000	0.74000000
560	0.60000000	0.66500000	0.70000000	0.73000000	0.74000000
550	0.58200000	0.63600000	0.66200000	0.69000000	0.70000000
540	0.56000000	0.60200000	0.62200000	0.64000000	0.65800000
530	0.53200000	0.56800000	0.59000000	0.60000000	0.61200000
520	0.50000000	0.52300000	0.53200000	0.54700000	0.55900000
510	0.45800000	0.47000000	0.47000000	0.48200000	0.49000000
500	0.42000000	0.42000000	0.42000000	0.42200000	0.43000000
490	0.37600000	0.37400000	0.36700000	0.36500000	0.37400000
480	0.33900000	0.33000000	0.31800000	0.31500000	0.31700000
470	0.30400000	0.28700000	0.27500000	0.26700000	0.26900000
460	0.27500000	0.25400000	0.23600000	0.22600000	0.22800000
450	0.25500000	0.22900000	0.20900000	0.19800000	0.19700000
440	0.24300000	0.21600000	0.19600000	0.18600000	0.18100000
430	0.23700000	0.21000000	0.19000000	0.17500000	0.17400000
420	0.23700000	0.21000000	0.18700000	0.17200000	0.16800000
410	0.23000000	0.20400000	0.18300000	0.16000000	0.16400000
400	0.23500000	0.20400000	0.18300000	0.16600000	0.16000000

ORIGINAL S MATRIX

0.00386306	0.00409196	0.00420660	0.00435443	0.00437453
0.00443538	0.00485211	0.00508079	0.00523517	0.00534480
0.00519913	0.00588750	0.00623636	0.00647040	0.00654532
0.00619343	0.00720993	0.00765475	0.00801551	0.00820221
0.00714383	0.00833549	0.00911866	0.00946087	0.00968124
0.00786921	0.00924551	0.00990675	0.01046962	0.01066427
0.00843201	0.00995247	0.01066427	0.01134831	0.01163941
0.00924551	0.01086253	0.01191053	0.01276236	0.01299963
0.01002146	0.01185581	0.01291014	0.01399365	0.01431961
0.01037364	0.01204845	0.01305964	0.01399365	0.01431961
0.00995247	0.01127019	0.01196551	0.01276236	0.01305964
0.00946087	0.01042152	0.01091267	0.01137447	0.01185581
0.00887015	0.00963676	0.01013750	0.01037364	0.01066427
0.00824007	0.00868823	0.00887015	0.00918187	0.00943911
0.00748051	0.00769008	0.00769008	0.00790553	0.00805251
0.00685379	0.00685379	0.00685379	0.00688543	0.00701344
0.00619343	0.00616497	0.00606640	0.00603853	0.00616497
0.00568763	0.00557097	0.00541915	0.00538184	0.00540669
0.00524724	0.00504581	0.00490830	0.00481871	0.00484096
0.00490830	0.00467661	0.00448674	0.00438461	0.00440485
0.00468739	0.00441500	0.00421630	0.00411084	0.00410139
0.00455965	0.00428481	0.00409196	0.00399881	0.00395304
0.00449708	0.00422602	0.00403581	0.00389880	0.00388983
0.00449708	0.00422602	0.00400803	0.00387196	0.00383646
0.00442518	0.00416803	0.00397129	0.00376644	0.00380129
0.00447642	0.00416803	0.00397129	0.00381884	0.00376644

TABLE IX

ABSORBANCE MATRIX OF 5 μg/ml F^- AND S ERROR MATRIX IN THE VISIBLE

pH / λ	4.0	4.5	5.0	5.5	6.0
650	0.20200000	0.21900000	0.23800000	0.25500000	0.26500000
640	0.26800000	0.29800000	0.32600000	0.34200000	0.34200000
630	0.34300000	0.37500000	0.42200000	0.44600000	0.43800000
620	0.43000000	0.47000000	0.51800000	0.54600000	0.53800000
610	0.48200000	0.53600000	0.59000000	0.61200000	0.60000000
600	0.52200000	0.57100000	0.62100000	0.65000000	0.63600000
590	0.55200000	0.60500000	0.65000000	0.68000000	0.66900000
580	0.59600000	0.64500000	0.69400000	0.73000000	0.71000000
570	0.63000000	0.68200000	0.73500000	0.76200000	0.75000000
560	0.63200000	0.68200000	0.73100000	0.75800000	0.74500000
550	0.60900000	0.65000000	0.68000000	0.70000000	0.69500000
540	0.58200000	0.60900000	0.63000000	0.65000000	0.64200000
530	0.54200000	0.56800000	0.59000000	0.60000000	0.60000000
520	0.50200000	0.52000000	0.53000000	0.53600000	0.54000000
510	0.45500000	0.46000000	0.46500000	0.46400000	0.47100000
500	0.41000000	0.40800000	0.40500000	0.40600000	0.41000000
490	0.36500000	0.36200000	0.35200000	0.34800000	0.35500000
480	0.32600000	0.31800000	0.30200000	0.29600000	0.30300000
470	0.28800000	0.27700000	0.25800000	0.25000000	0.25700000
460	0.26000000	0.24400000	0.22200000	0.21200000	0.22000000
450	0.24000000	0.22100000	0.19800000	0.19000000	0.19400000
440	0.23100000	0.21000000	0.18700000	0.17400000	0.18000000
430	0.22600000	0.20700000	0.18200000	0.17000000	0.17400000
420	0.22600000	0.20000000	0.18200000	0.16700000	0.17400000
410	0.22000000	0.19600000	0.17500000	0.16700000	0.16000000
400	0.23500000	0.20600000	0.18500000	0.17100000	0.16700000

ORIGINAL S MATRIX

0.00414888	0.00431451	0.00450745	0.00468739	0.00479657
0.00482982	0.00517525	0.00551990	0.00572705	0.00572705
0.00574025	0.00617918	0.00688543	0.00727664	0.00714383
0.00701344	0.00769008	0.00858877	0.00916075	0.00899355
0.00790553	0.00895223	0.01013750	0.01066427	0.01037364
0.00866824	0.00970356	0.01088757	0.01163941	0.01127019
0.00928819	0.01049376	0.01163941	0.01247186	0.01215993
0.01027853	0.01150618	0.01288045	0.01399365	0.01336383
0.01111555	0.01252942	0.01415569	0.01506368	0.01465315
0.01116686	0.01252942	0.01402591	0.01492558	0.01448542
0.01059086	0.01163941	0.01247186	0.01305964	0.01291014
0.00995247	0.01059086	0.01111555	0.01163941	0.01142697
0.00907676	0.00963676	0.01013750	0.01037364	0.01037364
0.00827811	0.00862842	0.00882940	0.00895223	0.00903506
0.00742901	0.00751504	0.00760206	0.00758457	0.00770781
0.00669778	0.00666701	0.00662111	0.00663638	0.00669778
0.00603853	0.00599696	0.00586045	0.00580672	0.00590107
0.00551990	0.00541915	0.00522313	0.00515147	0.00523517
0.00505744	0.00493096	0.00471988	0.00463373	0.00470903
0.00474167	0.00457016	0.00434441	0.00424552	0.00432445
0.00452826	0.00433442	0.00411084	0.00403581	0.00407316
0.00443538	0.00422602	0.00400803	0.00388983	0.00394395
0.00438461	0.00419692	0.00396215	0.00385417	0.00388983
0.00438461	0.00417982	0.00396215	0.00382764	0.00388983
0.00432445	0.00409196	0.00389880	0.00382764	0.00376644
0.00447642	0.00418727	0.00398962	0.00386306	0.00382764

TABLE X

ABSORBANCE MATRIX OF 10 μg/ml F^- AND S ERROR MATRIX IN THE VISIBLE

λ	pH 4.0	4.5	5.0	5.5	6.0
650	0.19200000	0.22400000	0.23200000	0.24400000	0.25000000
640	0.25700000	0.30000000	0.32000000	0.33600000	0.34200000
630	0.33000000	0.39000000	0.42000000	0.44200000	0.44500000
620	0.41000000	0.48000000	0.51500000	0.53200000	0.55200000
610	0.47500000	0.55000000	0.58200000	0.60800000	0.62800000
600	0.52000000	0.59000000	0.62000000	0.64800000	0.66000000
590	0.55200000	0.62000000	0.65000000	0.67600000	0.69500000
580	0.59400000	0.66000000	0.69800000	0.72400000	0.74600000
570	0.62900000	0.69900000	0.73800000	0.76000000	0.79000000
560	0.63700000	0.70000000	0.73000000	0.75600000	0.78000000
550	0.61800000	0.66200000	0.68500000	0.70800000	0.73000000
540	0.59100000	0.62400000	0.63800000	0.65200000	0.67500000
530	0.55800000	0.58600000	0.59200000	0.60200000	0.62100000
520	0.52000000	0.53200000	0.53500000	0.54500000	0.56000000
510	0.47200000	0.47600000	0.47000000	0.47800000	0.48800000
500	0.43000000	0.42200000	0.41400000	0.41800000	0.42200000
490	0.38500000	0.37000000	0.36000000	0.36000000	0.36200000
480	0.34300000	0.32600000	0.31100000	0.31000000	0.30500000
470	0.30600000	0.28500000	0.26700000	0.26200000	0.25600000
460	0.27600000	0.25200000	0.23000000	0.22400000	0.21600000
450	0.25500000	0.22700000	0.20600000	0.20000000	0.19000000
440	0.24500000	0.21700000	0.19500000	0.18700000	0.17600000
430	0.24200000	0.21400000	0.19200000	0.18200000	0.16800000
420	0.24200000	0.21400000	0.19200000	0.18200000	0.16800000
410	0.24200000	0.20900000	0.19000000	0.18000000	0.16100000
400	0.23900000	0.21400000	0.19000000	0.18000000	0.16500000

ORIGINAL S MATRIX

0.00405444	0.00436447	0.00444561	0.00457016	0.00463373
0.00470903	0.00519913	0.00544416	0.00564847	0.00572705
0.00557097	0.00639633	0.00685379	0.00720993	0.00725991
0.00669778	0.00786921	0.00852965	0.00887015	0.00928819
0.00777913	0.00924551	0.00995247	0.01056650	0.01106448
0.00862842	0.01013750	0.01086253	0.01158593	0.01191053
0.00928819	0.01086253	0.01163941	0.01235751	0.01291014
0.01023131	0.01191053	0.01299963	0.01380165	0.01451881
0.01108999	0.01302960	0.01425381	0.01499447	0.01606686
0.01129617	0.01305964	0.01399365	0.01485700	0.01570114
0.01081262	0.01196551	0.01261627	0.01330243	0.01399365
0.01016087	0.01096304	0.01132221	0.01169314	0.01232909
0.00941740	0.01004456	0.01018430	0.01042152	0.01088757
0.00862842	0.00887015	0.00893164	0.00913968	0.00946087
0.00772558	0.00779706	0.00769008	0.00783305	0.00801551
0.00701344	0.00688543	0.00675976	0.00682230	0.00688543
0.00632311	0.00610845	0.00596941	0.00596941	0.00599696
0.00574025	0.00551990	0.00533250	0.00532024	0.00525934
0.00527146	0.00502263	0.00481871	0.00476355	0.00469820
0.00491961	0.00465512	0.00442518	0.00436447	0.00428481
0.00468739	0.00439472	0.00418727	0.00412982	0.00403581
0.00458069	0.00429468	0.00408255	0.00400803	0.00390779
0.00454916	0.00426512	0.00405444	0.00396215	0.00383646
0.00454916	0.00426512	0.00405444	0.00396215	0.00383646
0.00454916	0.00421630	0.00403581	0.00394395	0.00377512
0.00451784	0.00426512	0.00403581	0.00394395	0.00381005

TABLE XI

ABSORBANCE MATRIX OF 15 μg/ml F^- AND S ERROR MATRIX IN THE VISIBLE

λ	pH 4.0	4.5	5.0	5.5	6.0
650	0.18400000	0.22300000	0.23200000	0.25400000	0.26200000
640	0.24200000	0.30700000	0.31400000	0.34500000	0.35800000
630	0.31400000	0.39200000	0.40000000	0.44000000	0.46000000
620	0.39100000	0.48200000	0.49000000	0.54800000	0.56700000
610	0.44900000	0.55000000	0.56000000	0.61000000	0.63400000
600	0.49500000	0.59000000	0.59800000	0.64000000	0.67000000
590	0.52100000	0.62000000	0.62600000	0.67200000	0.70000000
580	0.56100000	0.66000000	0.67000000	0.72000000	0.74500000
570	0.56100000	0.69800000	0.70800000	0.75800000	0.78800000
560	0.60200000	0.69700000	0.70200000	0.75000000	0.77000000
550	0.59100000	0.65400000	0.66200000	0.70000000	0.72000000
540	0.56200000	0.61800000	0.62000000	0.64600000	0.66200000
530	0.53800000	0.57500000	0.58000000	0.60000000	0.61100000
520	0.50000000	0.52500000	0.52800000	0.53800000	0.55000000
510	0.45800000	0.46300000	0.46500000	0.46800000	0.47200000
500	0.41700000	0.41500000	0.41200000	0.41000000	0.41200000
490	0.37500000	0.36100000	0.36200000	0.35500000	0.35400000
480	0.33500000	0.31700000	0.31500000	0.30300000	0.30000000
470	0.30200000	0.27500000	0.27500000	0.26000000	0.25100000
460	0.27300000	0.24200000	0.23900000	0.22100000	0.21200000
450	0.25400000	0.22000000	0.21800000	0.19700000	0.18800000
440	0.24400000	0.20700000	0.20500000	0.18700000	0.17500000
430	0.24000000	0.20500000	0.20200000	0.18200000	0.17100000
420	0.24000000	0.20500000	0.20200000	0.18200000	0.16800000
410	0.24000000	0.20400000	0.20200000	0.17900000	0.16800000
400	0.24000000	0.20500000	0.20000000	0.17900000	0.17400000

ORIGINAL S MATRIX

0.00398044	0.00435443	0.00444561	0.00467661	0.00476355
0.00454916	0.00528361	0.00536947	0.00576675	0.00594198
0.00536947	0.00642586	0.00654532	0.00717680	0.00751504
0.00641108	0.00790553	0.00805251	0.00920303	0.00961460
0.00732708	0.00924551	0.00946087	0.01061527	0.01127019
0.00814575	0.01013750	0.01032597	0.01137447	0.01210796
0.00864831	0.01086253	0.01101364	0.01224422	0.01305964
0.00948268	0.01191053	0.01218796	0.01367512	0.01448542
0.00948268	0.01299963	0.01330243	0.01492558	0.01599304
0.01042152	0.01296973	0.01311992	0.01465315	0.01534373
0.01016087	0.01174711	0.01196551	0.01305964	0.01367512
0.00950454	0.01081262	0.01086253	0.01153270	0.01196551
0.00899355	0.00979335	0.00990675	0.01037364	0.01063974
0.00824007	0.00872833	0.00878883	0.00899355	0.00924551
0.00748051	0.00756713	0.00760206	0.00765475	0.00772558
0.00680661	0.00677534	0.00672870	0.00669778	0.00672870
0.00617918	0.00598317	0.00599696	0.00590107	0.00588750
0.00563548	0.00540669	0.00538184	0.00523517	0.00519913
0.00522313	0.00490830	0.00490830	0.00474167	0.00464442
0.00488575	0.00454916	0.00451784	0.00433442	0.00424552
0.00467661	0.00432445	0.00430458	0.00410139	0.00401727
0.00457016	0.00419692	0.00417764	0.00400803	0.00389880
0.00452826	0.00417764	0.00414888	0.00396215	0.00386306
0.00452826	0.00417764	0.00414888	0.00396215	0.00383646
0.00452826	0.00416803	0.00414888	0.00393488	0.00383646
0.00452826	0.00417764	0.00412982	0.00393488	0.00388983

TABLE XII

ABSORBANCE MATRIX OF 20 μg/ml F^- AND S ERROR MATRIX IN THE VISIBLE

λ \ pH	4.0	4.5	5.0	5.5	6.0
650	0.14800000	0.21000000	0.24600000	0.27100000	0.27800000
640	0.19500000	0.29500000	0.33700000	0.37100000	0.38100000
630	0.25500000	0.38000000	0.43800000	0.48000000	0.49000000
620	0.32000000	0.45500000	0.53000000	0.58200000	0.59100000
610	0.37500000	0.52000000	0.59500000	0.64000000	0.65800000
600	0.41800000	0.55800000	0.62400000	0.67000000	0.68800000
590	0.45000000	0.59000000	0.65200000	0.70000000	0.71400000
580	0.48100000	0.63000000	0.71500000	0.75000000	0.76000000
570	0.51500000	0.66500000	0.75000000	0.78500000	0.80000000
560	0.53000000	0.66500000	0.73000000	0.77000000	0.78000000
550	0.52200000	0.62900000	0.68200000	0.70900000	0.72000000
540	0.50600000	0.59000000	0.62000000	0.64700000	0.65800000
530	0.48600000	0.55000000	0.57000000	0.59800000	0.60200000
520	0.45400000	0.49800000	0.51000000	0.53000000	0.53800000
510	0.42500000	0.44000000	0.44800000	0.45800000	0.46200000
500	0.39000000	0.39000000	0.38500000	0.39500000	0.40400000
490	0.35600000	0.34400000	0.33200000	0.34000000	0.34400000
480	0.32600000	0.30000000	0.28500000	0.28600000	0.29300000
470	0.29800000	0.26300000	0.24000000	0.24200000	0.24400000
460	0.27600000	0.23000000	0.20700000	0.20400000	0.20600000
450	0.26100000	0.21000000	0.18800000	0.18300000	0.18300000
440	0.25400000	0.20100000	0.17800000	0.17200000	0.17200000
430	0.25400000	0.19800000	0.17500000	0.16800000	0.16800000
420	0.25400000	0.19500000	0.17500000	0.16800000	0.16800000
410	0.24200000	0.19500000	0.17100000	0.16300000	0.16300000
400	0.24200000	0.19500000	0.17600000	0.17000000	0.17000000

ORIGINAL S MATRIX

0.00366379	0.00422602	0.00459125	0.00486330	0.00494232
0.00408255	0.00513962	0.00566149	0.00612253	0.00626514
0.00468739	0.00625073	0.00714383	0.00786921	0.00805251
0.00544416	0.00742901	0.00882940	0.00995247	0.01016087
0.00617918	0.00862842	0.01025489	0.01137447	0.01185581
0.00682230	0.00941740	0.01096304	0.01218796	0.01270372
0.00734397	0.01013750	0.01169314	0.01305964	0.01348749
0.00788735	0.01111555	0.01351858	0.01465315	0.01499447
0.00852965	0.01204845	0.01465315	0.01588295	0.01644111
0.00882940	0.01204845	0.01399365	0.01534373	0.01570114
0.00866824	0.01108999	0.01252942	0.01330243	0.01367512
0.00835470	0.01013750	0.01086253	0.01155929	0.01185581
0.00797868	0.00924551	0.00968124	0.01032597	0.01042152
0.00741193	0.00820221	0.00843201	0.00882940	0.00899355
0.00693316	0.00717680	0.00731023	0.00748051	0.00754972
0.00639633	0.00639633	0.00632311	0.00647040	0.00660589
0.00591468	0.00575349	0.00559669	0.00570074	0.00575349
0.00551990	0.00519913	0.00502263	0.00503421	0.00508079
0.00517525	0.00477453	0.00452826	0.00454916	0.00457016
0.00491961	0.00442518	0.00419692	0.00416803	0.00418727
0.00475260	0.00422602	0.00401727	0.00397129	0.00397129
0.00467661	0.00413934	0.00392583	0.00387196	0.00387196
0.00467661	0.00411084	0.00389880	0.00383646	0.00383646
0.00467661	0.00408255	0.00389880	0.00383646	0.00383646
0.00454916	0.00408255	0.00386306	0.00379255	0.00379255
0.00454916	0.00408255	0.00390779	0.00385417	0.00385417

TABLE XIII

ABSORBANCE MATRIX FOR $Ce^{(III)}$-ALIZARIN COMPLEXONE AND S ERROR MATRIX IN THE UV

pH / λ	4.0	4.5	5.0	5.5	6.0
300	0.46500000	0.46800000	0.43500000	0.44000000	0.43500000
295	0.53000000	0.52500000	0.48400000	0.49200000	0.49200000
290	0.60900000	0.60000000	0.56000000	0.59000000	0.59200000
285	0.72000000	0.72800000	0.70000000	0.76500000	0.79000000
280	0.84000000	0.88500000	0.87000000	1.00000000	1.04000001
275	0.94000000	1.01000001	0.98400000	1.15000001	1.20000000
270	1.03000000	1.09000000	1.05000000	1.25000000	1.30000000
265	1.09999999	1.12000000	1.05000000	1.25000000	1.30000000
260	1.09999999	1.08000000	1.00000000	1.09999999	1.12000000
255	1.02000000	0.98000000	0.88000000	0.94000000	0.94000000
250	0.92000000	0.86000000	0.76000000	0.78000000	0.76200000
245	0.80500000	0.75800000	0.67000000	0.68000000	0.66200000
240	0.77000000	0.71800000	0.64000000	0.65000000	0.63800000
235	0.86400000	0.80000000	0.70000000	0.70500000	0.69000000
230	1.18000001	1.08000000	0.90000000	0.91800000	0.89800000

ORIGINAL S MATRIX

0.00760206	0.00765475	0.00709465	0.00717680	0.00709465
0.00882940	0.00872833	0.00794202	0.00808967	0.00808967
0.01059086	0.01037364	0.00946087	0.01013750	0.01018430
0.01367512	0.01392936	0.01305964	0.01516810	0.01606686
0.01802732	0.01999544	0.01931662	0.02605740	0.02857137
0.02269505	0.02666435	0.02511488	0.03680706	0.04129820
0.02792101	0.03205760	0.02923688	0.04633734	0.05199135
0.03280432	0.03435034	0.02923688	0.04633734	0.05199135
0.03280432	0.03132788	0.02605740	0.03280432	0.03435034
0.02728545	0.02488462	0.01976656	0.02269505	0.02269505
0.02167360	0.01887692	0.01499447	0.01570114	0.01506368
0.01663149	0.01492558	0.01218796	0.01247186	0.01196551
0.01534373	0.01361229	0.01137447	0.01163941	0.01132221
0.01905158	0.01644111	0.01305964	0.01321086	0.01276236
0.03943947	0.03132788	0.02069813	0.02157402	0.02060303

TABLE XIV

ABSORBANCE MATRIX OF 2 μg/ml F^- AND S
ERROR MATRIX IN THE UV

λ \ pH	4.0	4.5	5.0	5.5	6.0
300	0.42000000	0.42000000	0.41000000	0.41200000	0.41800000
295	0.49500000	0.49500000	0.48600000	0.48900000	0.49000000
290	0.63500000	0.65800000	0.65400000	0.64500000	0.64800000
285	0.88500000	0.98000000	0.98600000	0.99000000	0.98800000
280	1.09999999	1.23999999	1.25000000	1.26000001	1.27000000
275	1.15000001	1.26000001	1.30000000	1.31000000	1.33000000
270	1.15000001	1.26000001	1.26000001	1.27000000	1.28000000
265	1.08000000	1.09999999	1.09999999	1.09999999	1.12000000
260	1.00000000	0.95000000	0.93000000	0.93500000	0.93500000
255	0.88200000	0.80200000	0.78200000	0.77800000	0.77500000
250	0.78800000	0.71800000	0.67500000	0.66600000	0.66000000
245	0.72000000	0.66000000	0.63000000	0.62000000	0.61200000
240	0.72000000	0.68600000	0.64200000	0.63200000	0.62200000
235	0.85000000	0.80500000	0.74200000	0.71000000	0.70500000
230	1.18000001	1.12000000	1.01000001	0.94000000	0.92000000

ORIGINAL S MATRIX

0.00685379	0.00685379	0.00669778	0.00672870	0.00682230
0.00814575	0.00814575	0.00797868	0.00803399	0.00805251
0.01124427	0.01185581	0.01174711	0.01150618	0.01158593
0.01999544	0.02488462	0.02523080	0.02546426	0.02534726
0.03280432	0.04528257	0.04633734	0.04741667	0.04852115
0.03680706	0.04741667	0.05199135	0.05320238	0.05570973
0.03680706	0.04741667	0.04741667	0.04852115	0.04965135
0.03132788	0.03280432	0.03280432	0.03280432	0.03435034
0.02605740	0.02322368	0.02217844	0.02243526	0.02243526
0.01985780	0.01651700	0.01577361	0.01562900	0.01552141
0.01599304	0.01361229	0.01232909	0.01207622	0.01191053
0.01367512	0.01191053	0.01111555	0.01086253	0.01066427
0.01367512	0.01264536	0.01142697	0.01116686	0.01091267
0.01844723	0.01663149	0.01438570	0.01336383	0.01321086
0.03943947	0.03435034	0.02666435	0.02269505	0.02167360

TABLE XV

ABSORBANCE MATRIX OF 5 μg/ml F^- AND S
ERROR MATRIX IN THE UV

pH / λ	4.0	4.5	5.0	5.5	6.0
300	0.43200000	0.43200000	0.43000000	0.42700000	0.43000000
295	0.51600000	0.51800000	0.51000000	0.50900000	0.51100000
290	0.65000000	0.68000000	0.68000000	0.67800000	0.68000000
285	0.90500000	1.02000000	1.04000001	1.04000001	1.04000001
280	1.14000000	1.29000001	1.31999999	1.34000000	1.33000000
275	1.17000000	1.33000000	1.34999999	1.34999999	1.37000000
270	1.17000000	1.28000000	1.30000000	1.31000000	1.31999999
265	1.09000000	1.12000000	1.12000000	1.12000000	1.11000000
260	1.00000000	0.96000000	0.91500000	0.92800000	0.92000000
255	0.86500000	0.81000000	0.78800000	0.77500000	0.72000000
250	0.77000000	0.70000000	0.68000000	0.66500000	0.65800000
245	0.71000000	0.66000000	0.65000000	0.63000000	0.63000000
240	0.72000000	0.69000000	0.66000000	0.65000000	0.64000000
235	0.86000000	0.81800000	0.77000000	0.74000000	0.73000000
230	1.20000000	1.13000000	1.04000001	0.97800000	0.94000000

ORIGINAL S MATRIX

0.00704581	0.00704581	0.00701344	0.00696516	0.00701344
0.00854931	0.00858877	0.00843201	0.00841262	0.00845145
0.01163941	0.01247186	0.01247186	0.01241455	0.01247186
0.02093780	0.02728545	0.02857137	0.02857137	0.02857137
0.03596922	0.05080788	0.05444162	0.05700738	0.05570973
0.03854172	0.05570973	0.05833525	0.05833525	0.06108451
0.03854172	0.04965135	0.05199135	0.05320238	0.05444162
0.03205760	0.03435034	0.03435034	0.03435034	0.03356843
0.02605740	0.02376463	0.02142551	0.02207654	0.02167360
0.01909550	0.01682407	0.01599304	0.01552141	0.01367512
0.01534373	0.01305964	0.01247186	0.01204845	0.01185581
0.01336383	0.01191053	0.01163941	0.01111555	0.01111555
0.01367512	0.01276236	0.01191053	0.01163941	0.01137447
0.01887692	0.01713685	0.01534373	0.01431961	0.01399365
0.04129820	0.03515046	0.02857137	0.02477029	0.02269505

TABLE XVI

ABSORBANCE MATRIX OF 10 μg/ml F^- AND S
ERROR MATRIX IN THE UV

λ	pH 4.0	4.5	5.0	5.5	6.0
300	0.43800000	0.43200000	0.42900000	0.42800000	0.45000000
295	0.51600000	0.51500000	0.51200000	0.50800000	0.53200000
290	0.64800000	0.68000000	0.68000000	0.68000000	0.70200000
285	0.89000000	1.02000000	1.05000000	1.05000000	1.06999999
280	1.09999999	1.30000000	1.34999999	1.34000000	1.39000000
275	1.16000000	1.34000000	1.36000000	1.34000000	1.40000001
270	1.17000000	1.30000000	1.33000000	1.33000000	1.34999999
265	1.11000000	1.12000000	1.13000000	1.14000000	1.15000001
260	1.01000001	0.96000000	0.94000000	0.94000000	0.96000000
255	0.88500000	0.80800000	0.78800000	0.77900000	0.80000000
250	0.74800000	0.70200000	0.67800000	0.66900000	0.69200000
245	0.72800000	0.66100000	0.64000000	0.63000000	0.65800000
240	0.73000000	0.69000000	0.66200000	0.65000000	0.68000000
235	0.86000000	0.81800000	0.77000000	0.74000000	0.76000000
230	1.20000000	1.15000001	1.04000001	0.97800000	0.98000000

ORIGINAL S MATRIX

0.00714383	0.00704581	0.00699731	0.00698122	0.00734397
0.00854931	0.00852965	0.00847093	0.00839327	0.00887015
0.01158593	0.01247186	0.01247186	0.01247186	0.01311992
0.02022698	0.02728545	0.02923688	0.02923688	0.03061477
0.03280432	0.05199135	0.05833525	0.05700738	0.06396333
0.03766440	0.05700738	0.05969405	0.05700738	0.06545323
0.03854172	0.05199135	0.05570973	0.05570973	0.05833525
0.03356843	0.03435034	0.03515046	0.03596922	0.03680706
0.02666435	0.02376463	0.02269505	0.02269505	0.02376463
0.01999544	0.01674677	0.01599304	0.01566502	0.01644111
0.01458583	0.01311992	0.01241455	0.01215993	0.01282127
0.01392936	0.01193799	0.01137447	0.01111555	0.01185581
0.01399365	0.01276236	0.01196551	0.01163941	0.01247186
0.01887692	0.01713685	0.01534373	0.01431961	0.01499447
0.04129820	0.03680706	0.02857137	0.02477029	0.02488462

TABLE XVII

ABSORBANCE MATRIX OF 15 µg/ml F^- AND S
ERROR MATRIX IN THE UV

pH	4.0	4.5	5.0	5.5	6.0
λ					
300	0.45400000	0.42900000	0.42200000	0.42000000	0.42100000
295	0.53000000	0.51000000	0.50500000	0.50200000	0.50200000
290	0.65500000	0.67200000	0.67500000	0.68000000	0.67500000
285	0.88000000	1.00000000	1.04000001	1.05000000	1.05000000
280	1.09000000	1.26000001	1.34000000	1.34000000	1.34000000
275	1.16000000	1.30000000	1.34999999	1.36000000	1.37000000
270	1.17000000	1.25000000	1.30000000	1.31000000	1.31999999
265	1.14000000	1.11000000	1.09999999	1.11000000	1.11000000
260	1.05000000	0.94200000	0.93000000	0.92000000	0.92000000
255	0.92000000	0.80000000	0.78200000	0.76800000	0.75800000
250	0.81500000	0.69000000	0.67100000	0.66000000	0.65000000
245	0.75000000	0.65200000	0.63300000	0.62200000	0.61600000
240	0.75000000	0.68200000	0.66000000	0.74100000	0.63200000
235	0.89000000	0.81000000	0.77000000	0.73800000	0.71800000
230	1.22000000	1.11000000	1.04000001	0.97000000	0.92500000

ORIGINAL S MATRIX

0.00741193	0.00699731	0.00688543	0.00685379	0.00686959
0.00882940	0.00843201	0.00833549	0.00827811	0.00827811
0.01177419	0.01224422	0.01232909	0.01247186	0.01232909
0.01976656	0.02605740	0.02857137	0.02923688	0.02923688
0.03205760	0.04741667	0.05700738	0.05700738	0.05700738
0.03766440	0.05199135	0.05833525	0.05969405	0.06108451
0.03854172	0.04633734	0.05199135	0.05320238	0.05444162
0.03596922	0.03356843	0.03280432	0.03356843	0.03356843
0.02923688	0.02279980	0.02217844	0.02167360	0.02167360
0.02167360	0.01644111	0.01577361	0.01527324	0.01492558
0.01701888	0.01276236	0.01221606	0.01191053	0.01163941
0.01465315	0.01169314	0.01119260	0.01091267	0.01076294
0.01465315	0.01252942	0.01191053	0.01435262	0.01116686
0.02022698	0.01682407	0.01534373	0.01425381	0.01361229
0.04324452	0.03356843	0.02857137	0.02431818	0.02192457

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APPENDIX A

RANK OF MATRIX

```
$ID          B-0001          EL RAWI
$JOB                         EL RAWI                2211-50006
$IBJOB NAMEPR
$IBFTC DKNAME  NODECK
C     ANALYSIS OF SPECTRA                                  KATZ-WALLACE
C
C     GIVEN -N- EXPERIMENTS IN EACH OF WHICH THE OPTICAL ABSORPTION
C     IS MEASURED AT -L- WAVELENGTHS RESULTING IN MATRIX
C     -A- WITH L ROWS AND N COLUMNS.  DIMENSION A(50,20)
C          (L MUST BE G.T.E. N)
C
C     OBJECT - TO DETERMINE RANK OF MATRIX,TAKING INTO ACCOUNT
C     EXPERIMENTAL ERRORS IN -S- MATRIX
C
C     METHOD-REDUCE ALL ELEMENTS BELOW PRINCIPAL DIAGONAL TO ZERO
C     AFTER MAXIMUM (PIVOT) PLACED ON DIAGONAL
C
C     INPUT-
C          CARD 1 - N          COLS. 1-5
C                   L          COLS. 6-10
C                   CRIT       COLS. 11-19    (F9.8)
C     CRIT IS THE CRITERION FOR SETTING A ELEMENTS TO ZERO
C               IF A(I,J) L.T. CRIT*S(I,J),A(I,J)=0.0
C
C          EXPERIMENT 1 DATA STARTS ON CARD 2 AND CONTINUES AS NEEDED
C                   8 WAVELENGTHS PER CARD, 9 COLUMNS PER WAVELENGTH
C                   FOR EACH WAVELENGTH- 5 DIGIT A(I,J) COLS. 1,10,19,
C                        28,37,46,55,64 (NO DECIMAL POINT,WITH SIGN)
C                                       2 DIGIT S(I,J) COLS.7,16,25
C                        34,43,52,61,70   (NO DECIMAL POINT)
C          EXPERIMENT 2 DATA FOLLOWS IMMEDIATELY AND SO ON
C
C
      DIMENSIONA(35,18),S(35,18)
C
    1 FORMAT(2I5,F9.8)
    2 FORMAT(16(F5.3))
    3 FORMAT (     1H2,10X,17HRANK OF SYSTEM IS,I3,1X,31HWITHIN A RANGE O
     1 OF PLUS OR MINUS,F15.5,1X,12HSIGMA LIMITS)
    4 FORMAT(1H1,30X,17HORIGINAL A MATRIX//)
    5 FORMAT (1H1,30X,17HORIGINAL S MATRIX//)
    6 FORMAT (1H1,30X,16HREDUCED A MATRIX//)
    7 FORMAT (1H1,30X,16HREDUCED S MATRIX//)
8     FORMAT(1HJ,12F11.9)
      READ(5,1)N,L,CRIT
   50 CONTINUE
      DO10J=1,N
   10 READ(5,2) (A(I,J),I=1,L)
      REWIND  1
      WRITE  (1) A
      END FILE 1
      F=.006
      REWIND 1
      DO 14 I=1,L
```

```
      DO 14 J=1,N
      X=A(I,J)
   14 S(I,J)=.43429*T*10.**X
      WRITE(6,4)
      DO20I=1,L
   20 WRITE(6,8)(A(I,J),J=1,N)
      WRITE(6,5)
      DO30I=1,L
   30 WRITE(6,8)(S(I,J),J=1,N)
C
C     MATRIX ELEMENTS READ IN,NOW TO PIVOT AND REDUCE ROWS
C
      NMIN=N-1
      DO140JC=1,NMIN
      AMAX=0.0
      DO110I=JC,L
      DO110J=JC,N
      IF(AMAX-ABS(A(I,J)).GE.0.)GO TO 110
  105 AMAX=ABS(A(I,J))
      IMAX=I
      JMAX=J
  110 CONTINUE
      IF(AMAX.LE.0.)GO TO 150
  112 DO115 J=1,N
      SW=A(JC,J)
      A(JC,J)=A(IMAX,J)
      A(IMAX,J)=SW
      SW=S(JC,J)
      S(JC,J)=S(IMAX,J)
  115 S(IMAX,J)=SW
      DO120I=1,L
      SW=A(I,JC)
      A(I,JC)=A(I,JMAX)
      A(I,JMAX)=SW
      SW=S(I,JC)
      S(I,JC)=S(I,JMAX)
  120 S(I,JMAX)=SW
C
C     PIVOT ELEMENT PLACED. REDUCE SUB-PIVOT ELEMENTS TO ZERO
      IPLUS=JC+1
      DO130I=IPLUS,L
      IF(A(I,JC).EQ.0.)GO TO 130
  125 FAC=A(I,JC)/A(JC,JC)
      DO129 J=IPLUS,N
      A(I,J)=A(I,J)-FAC*A(JC,J)
      TEMP=A(JC,J)/A(JC,JC)
      S(I,J)=SQRT(S(I,J)**2+(S(I,JC)*TEMP)**2+(S(JC,J)*FAC)**2+(S(JC,JC)
     1*FAC*TEMP)**2)
      IF(ABS(A(I,J))-ABS(CRIT*S(I,J)).GT.0.) GO TO 129
  127 A(I,J)=0.0
  129 CONTINUE
      A(I,JC)=0.0
      S(I,JC)=0.0
  130 CONTINUE
```

```
  140 CONTINUE
      IF(A(N,N).NE.0.)GO TO 150
  142 IF(L-N.LE.0)GOTO150
  143 NPLUS=N+1
      DO145 I=NPLUS,L
      IF(A(I,N).EQ.0.)GO TO 145
  144 SW=A(N,N)
      A(N,N)=A(I,N)
      A(I,N)=SW
      SW=S(N,N)
      S(N,N)=S(I,N)
      S(I,N)=SW
      GO TO 150
  145 CONTINUE
C
C     MATRIX IS REDUCED,DETERMINE RANK
C
  150 DO160I=1,N
      NRANK=N+1-I
      IF(ABS(A(NRANK,NRANK)).GE.3.*S(NRANK,NRANK))GOTO162
  160 CONTINUE
C
C     PRINT RANK REDUCED A AND S MATRICES
C
  162 WRITE(6,3)NRANK,CRIT
      WRITE(6,6)
      DO165I=1,L
  165 WRITE(6,8)(A(I,J),J=1,N)
      WRITE(6,7)
      DO170 I=1,L
  170 WRITE(6,8)(S(I,J),J=1,N)
      READ(1)A
      GO TO 50
      END
$ENTRY
      ABSORBANCE DATA
$IBSYS
```

APPENDIX B

PLOT PROGRAM

```
$ID          B-0001          EL RAWI
$JOB                         EL RAWI                2211-50006
$IBJOB NAMEPR  MAP
$IBFTC          NODECK
      DIMENSION X(75),Y(75),Z(75),XX(5),YY(15)
    1 FORMAT(16(F5.3))
    2 DO50I=1,5
   50 XX(I)=I
       YY(1)=.300
      DO 20  I=2,15
   20 YY(I)=YY(I-1)-.005
      DO 51 I=1,15
      Y(I)=YY(I)
   51 X(I)=XX(1)
      DO 52 I=16,30
      Y(I)=YY(I-15)
   52 X(I)=XX(2)
      DO 53  I=31,45
      Y(I)=YY(I-30)
   53 X(I)=XX(3)
      DO 54 I=46,60
      Y(I)=YY(I-45)
   54 X(I)=XX(4)
      DO55  I=61,75
      Y(I)=YY(I-60)
   55 X(I)=XX(5)
      L=1
      DO110I=1,5
      K=L+14
      READ(5,1)(Z(J),J=L,K)
  110 L=L+15
      CALL PLOT(X,1.0,6.0,0,Y,.300,.230,0,Z,0.0,2,0,0,75,1,1,3,3)
      GOTO2
      END
$IBFTC PLOT    NODECK
      SUBROUTINEPLOT(X,XMIN,XMAX,LX,Y,YMIN,YMAX,LY,Z,ZMIN,ZMAX,LZ,NPT,
     1NPLOT,NCOPY,NCD,NDIM)
      DIMENSION X(1),Y(1),Z(1),SX(6),TITLE(12),L(134),NCH(41),MOP(18)
    1 FORMAT(12A6)
    2 FORMAT(58A1,3A6,4A1)
    3 FORMAT(1H1,26X,12A6)
    4 FORMAT(1H ,A1,3X,F6.3,121A1)
    5 FORMAT(132A1)
    6 FORMAT(10X,F6.3,4(18X,F6.3))
    7 FORMAT(1PE17.2,E116.2)
    8 FORMAT(1PE17.2,E61.2,E55.2)
    9 FORMAT(1PE17.2,2E40.2,E36.2)
   10 FORMAT(1PE17.2,3E30.2,E26.2)
   11 FORMAT(1PE17.2,4E24.2,E20.2)
   12 FORMAT(1HK,62X,3A6)
      SLOG(F)=ALOG(F)/2.302585
      LLX=LX+1
      NDD=NCD+1
        GOTO(15,13,14,13),NDD
```

```
 13 READ(5,1)(TITLE(I),I=1,12)
 14 IF(NDD.GE.3)READ(5,2)(MOP(I),I=1,18),(NCH(I),I=1,40),TAB1,TAB2,TAB
   13,ND,NP,NM,NB
 15 NCH(41)=NB
    NPN=NPT/NPLOT
    IF(LX.GT.0)GOTO17
    CX=120./(XMAX-XMIN)
    SX(1)=XMIN
    SX( 6)=XMAX
    U=XMIN
    DO16 K=2,5
    U=(XMAX-XMIN)/ 5.+U
 16 SX(K)=U
    GOTO19
 17 XLX=LX
    CX=120./XLX
    NX=SLOG(XMIN)
    DO18K=1,LLX
 18 SX(K)=10.**(NX+K-1)
 19 CALLPOT(X,XMIN,LX,NPT,0,120.,CX)
    IF(LY.GT.0)GOTO20
    CY=50./(YMAX-YMIN)
    GOTO21
 20 YLY=LY
    CY=50./YLY
    KY=CY
    NY=SLOG(YMIN)
 21 CALLPOT(Y,YMIN,LY,NPT,1,50.,CY)
    IF(NDIM.LT.3)GOTO24
    IF(LZ.GT.0)GOTO22
    CZ=40./(ZMAX-ZMIN)
    GOTO23
 22 ZLZ=LZ
    CZ=40./ZLZ
 23 CALLPOT(Z,ZMIN,LZ,NPT,0,40.,CZ)
 24 DO50NN=1,NCOPY
    M1=1
    T1=33.
    LYY=LY
    TT=50.
    WRITE(6,3)(TITLE(I),I=1,12)
    DO43KK=1,51
    N=1
    NNN=NPN
    JED=1
    T=51-KK
    DO25J=1,133
 25 L(J)=NB
    L(133)=ND
    IF(LY.GT.0)GOTO26
    L(13)=NP
    IF(T.GT.TT)GOTO30
    SCALE=T/CY+YMIN
    L(133)=NP
```

```
      N=0
      TT=TT-5.
      IF(T.LE.0.)SCALE=YMIN
      GOTO30
   26 GOTO(27,27,28,28,27,28),LY
   27 SS=KY*LYY
      GOTO29
   28 SS=KY*LYY+1.
   29 L(13)=ND
      IF(T.GT.SS)GOTO30
      SCALE=10.**(NY+LYY)
      N=0
      LYY=LYY-1
      L(13)=NP
      L(133)=NP
   30 IF(50..EQ.T)GOTO31
      IF(0..NE.T)GOTO37
   31 DO32J=14,133
   32 L(J)=NM
      IF(LX.GT.0)GOTO34
      DO33J=13,133,24
   33 L(J)=NP
      GOTO36
   34 KX=120/LX
      DO35J=13,133,KX
   35 L(J)=NP
   36 IF(50..EQ.T)L(133)=ND
   37 DO40LM=1,NPLOT
      DO39I=JED,NNN
      IF(Y(I).NE.T)GOTO39
      J=X(I)
      IF(NDIM.NE.3)GOTO38
      IZ=Z(I)
      L(J+13)=NCH(IZ+1)
      GOTO39
   38 L(J+13)=NCH(LM)
   39 CONTINUE
      JED=NNN+1
      NNN=NNN+NPN
   40 CONTINUE
      IF(T1.NE.T)GOTO41
      IF(15..GE.T)GOTO41
      L(2)=MOP(M1)
      M1=M1+1
      T1=T1-1.
   41 IF(N.EQ.1)GOTO42
      WRITE(6,4)L(2),SCALE,(L(J),J=12,132)
      GOTO43
   42 WRITE(6,5)(L(J),J=1,132)
   43 CONTINUE
      GOTO(44,45,46,47,48,49,44),LLX
   44 WRITE(6,6)(SX(K),K=1,5)
      GOTO50
   45 WRITE(6,7)(SX(K),K=1,LLX)
```

```
      GOTO50
   46 WRITE(6,8)(SX(K),K=1,LLX)
      GOTO50
   47 WRITE(6,9)(SX(K),K=1,LLX)
      GOTO50
   48 WRITE(6,10)(SX(K),K=1,LLX)
      GOTO50
   49 WRITE(6,11)(SX(K),K=1,LLX)
   50 WRITE(6,12)TAB1,TAB2,TAB3
      RETURN
      END
$IBFTC POT
      SUBROUTINEPOT(V,VMIN,LV,NP,J,VC,C)
      DIMENSIONV(1)
      IF(LV.GT.0)GOTO2
      DO1I=1,NP
    1 V(I)=FLOAT(IFIX(C*(V(I)-VMIN)+.5))
       GOTO4
    2 DO3I=1,NP
    3 V(I)=FLOAT(IFIX(C*(ALOG(V(I)/VMIN)/2.302585)+.5))
    4 IF(J.GT.0)GOTO7
      DO6I=1,NP
      IF(V(I).LT.0.)GOTO5
      IF(V(I).LE.VC)GOTO6
    5 V(I)=VC+1.
    6 CONTINUE
    7 RETURN
      END
$ENTRY
      ABSORBANCE VERSES WAVELENGTH AND PH  F-CE-AC SYSTEM  15 MICRO GM.F
WAVELENGTH MICRONS*1234567890+ABCDEFGHIJKLMNOPQRSTUVWXYZ/$  PH 4.0-6.0  .+-
$IBSYS
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VITA

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Candidate for the Degree of

Master of Science

Thesis: THE pH AND CONCENTRATION EFFECT IN THE $Ce^{(III)}$-ALIZARIN COMPLEXONE FLUORIDE SYSTEM

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