COMPUTER INTERPRETATION OF SPECTROPHOTOMETRIC DATA OF HAFNIUM-

CHLORANILIC ACID COMPLEXES IN 3M PERCHLORIC ACID MEDIUM

By

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Bachelor of Science

Northwestern State College

Alva, Oklahoma

1962

Submitted to the faculty of the Graduate College of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1966

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PREFACE

In the area of analytical data interpretation computer applications
are becoming necessarily more and more frequent. The cause of this
phenomenon is a result of modern day analytical chemistry. More data of
a more complex nature are available for interpretation now than ever be-
fore. The computer can be a most helpful and powerful tool for the modern
analytical chemist in many areas of research.

This thesis presents several applications of computer analysis in
areas where manual interpretation of the large amount of data would re-
quire many hours of painstaking work. A study of the hafnium-chloranilic
acid complex system in three molar perchloric acid is presented in which
the computer is used for determining the number, metal to ligand ratio,
and formation constants of the complexes.

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CHAPTER I

INTRODUCTION

Many spectrophotometric methods used in quantitative analysis have been developed without a complete knowledge of the nature and properties of the absorbing species or the effect of many solution variables on the analysis. Unambiguous and straightforward methods for the determination of the number, nature and stabilities of several absorbing species in solution with related equilibria generally are not available. This thesis was concerned with the interpretation of spectrophotometric data in such a multicomponent system.

The hafnium-chloranilic acid complex system in three molar perchloric acid was studied in this work with the help of three computer programs. A large amount of spectrophotometric data was analyzed and interpreted on the basis of:

(1) The number of absorbing species found in the system.

(2) The ligand to metal ratio of the chloranilic acid-hafnium complexes.

(3) The formation constants of the complexes.

The continuous variation method of Job (5) was used also for comparison with earlier work done in this laboratory (13). In this work fluoride ion was added to the hafnium-chloranilic acid system in three molar perchloric acid solvent and some comparison with the earlier work was made.

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CHAPTER II

REVIEW OF THE LITERATURE

Chloranilic acid (1,4 dichloro-2,5 dihydroxyquinone), as a chromo-
genic agent in the determination of hafnium, is of considerable interest
because of its ability to form the colored complex at high acidities
where the hydrolysis of hafnium does not interfere. Previous studies
of hafnium (9,10) had shown that hydrolysis was negligible in 3M per-
chloric acid and this medium at 25°C was used throughout this work.

In studies on the zirconium chloranilate complex in 2M perchloric
medium, Thamer and Voigt (6) had found evidence for species containing
1 and 2 chloranilic acid groups per metal atom. The principal species
was the 1:1 complex with an absorption maximum at 328 mμ. Frost-Jones,
Yardley (4) and Bricker, Waterbury (2) had found that the absorbance of
the zirconium-chloranilic acid complex decreased markedly in the range
0-3.5M perchloric acid, but for the present studies of 1×10^{-4}M hafnium
in 3.0M perchloric acid sufficient intensity remained for the study to be
completed.

The masking effect of the fluoride ion upon highly acid, aqueous
solutions of the hafnium-chloranilic acid complexes had been established
previously. Varga and Hume (9) had found the formation constants of the
various hafnium fluoride complexes and it was assumed in this work that
they could be used to describe the behavior of hafnium (IV) and fluoride.
Varga, Zumwalt and Wyatt (13), using the continuous variation method of

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Job (5) and iterative machine calculations on a relatively small amount of data, had postulated the existence of two absorbing species of hafnium-chloranilic acid complexes, namely, species with chloranilic acid to hafnium mole ratios of 2:1 and 4:1.

Wallace and Katz (15) had developed a method for the determination of rank of a matrix in the analysis of absorption spectra of multicomponent systems. Earlier work by Wallace (14) and Ainsworth (1) also described methods by which the number of absorbing species in a system of absorbance data could be determined from matrix rank calculations. In this thesis the method of Wallace and Katz (15) was used exclusively for the determination of the number of species in solution from absorption data.

The machine calculation of formation constants of the hafnium-chloranilic acid complexes by least squares methods was based upon the work of Varga, Zumwalt and Wyatt (13).

The computer plotting subroutine used in this work had been developed by E. J. Kobetich, Department of Physics, Kansas State University, Manhattan, Kansas, in 1964. It was revised for use on the IBM 1410 by R. W. Whitney and C. F. Cromwell, Jr., at Oklahoma State University. Further modification of the routine for the IBM 7040 was completed by W. V. Accola, OSU Computer Center, Dr. L. P. Varga and the author.

CHAPTER III

EXPERIMENTAL

Reagents

Hafnium.

Potassium hexafluorohafnate, K_2HfF_6, had been prepared previously (9) from reactor grade hafnium metal manufactured by the Wah Chang Corporation. The major non-gaseous impurities were Zr 3%, Ta<200 p.p.m., Nb<100 p.p.m., and Fe 150-200 p.p.m. A 25 g. sample of stock K_2HfF_6 salt was dissolved in approximately 50 ml of 3M hydrofluoric acid at about 100° using a polypropylene beaker in a hot water bath (9). The Hf concentration at this point was about 0.8M. (8). The hot solution was then filtered rapidly through a coarse filter paper using a steam jacketed polypropylene funnel. After the filtrate cooled it was filtered, and the colorless, recrystallized K_2HfF_6 salt (mol. wt. 370.86) recovered, air dried, and stored in a desiccator.

A 0.03709 gram sample of the K_2HfF_6 was weighed into a platinum crucible, dissolved in 70% reagent grade perchloric acid and evaporated twice almost to dryness. The resulting mass was then dissolved in concentrated reagent grade hydrofluoric acid, evaporated almost to dryness, and again evaporated almost to dryness twice with 70% perchloric acid. The additional hydrofluoric acid fuming had been found in previous work to insure reproducible results, presumably by destroying hafnyl bonds present in the original salt. The mass was then dissolved in 3M

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perchloric acid and transferred quantitatively to a 100 ml volumetric flask to make a stock solution 1.00×10^{-3}M in hafnium. The solution was found to be stable for three to four days as described in the section Preparation of Solutions.

Chloranilic Acid.

Fisher certified reagent grade chloranilic acid, $C_6Cl_2H_2O_4$, mol. wt. 208.996 (lot #714466) was used throughout this work. Without further purification 0.02090 g of the chloranilic acid were weighed into a small beaker, transferred quantitatively to a 100 ml volumetric flask and made almost to volume with 3M perchloric acid. After shaking for two to three hours on a Burrell "wrist action" shaker at room temperature, complete dissolution seemed apparent due to the disappearance of any particles of the acid. The solution was then made exactly to volume with 3M perchloric acid and shaken once more for an hour giving a stock solution 1.00×10^{-3}M in chloranilic acid (henceforth referred to as H_2Ch). Attempts to prepare 5×10^{-3}M H_2Ch failed after 24 hours of shaking.

Perchloric Acid.

The 70-72% perchloric acid used throughout the work was Baker's Analyzed Reagent grade. A stock solution of about 5M was prepared by diluting the concentrated acid with distilled water which had been passed through a bed of Fisher mixed cation and anion exchange resin, Rexyn*RG502 (H-OH). The 5M acid was then standardized against primary standard sodium carbonate and subsequently diluted to exactly 3.00M in a 2 liter volumetric flask.

Hydrofluoric Acid.

The hydrofluoric acid used in this work was Bakers Analyzed Reagent grade, 48.7% HF. The reagent was handled at all times in Nalgene or other

plastic ware.

Apparatus

Spectrophotometers.

The Beckman DK-1 spectrophotometer used in this work consisted of the basic DK-1 with a Brown strip-chart recorder. The hydrogen lamp source was used for all measurements made in the UV range. The slit width was set at 0.2 mm.

The battery powered Beckman DU fitted with a photomultiplier attachment gave the necessary stability and reproducibility required for precision measurements in the latter part of this work. A hydrogen lamp was used throughout. The slit width maintained on the DU was 0.2 mm.

Glass and Plastic Ware.

All glassware used was Pyrex and volumetric glassware met A.C.S. requirements for precision and accuracy. Plastic ware used was Nalgene, polyethylene, polypropylene and polystyrene. Nalgene pipets and calibrated tubes were used for volumetric work. A polystyrene buret, available from Fisher Scientific Company, was used for accurately dispensing fluoride solutions.

Cells.

One cm matched silica cells were used throughout this work for both the DK-1 and DU. Etching of the cells by F^-, which ranged up to about $2 \times 10^{-4} M$, was not discernible, either by eye or instrumental means.

Computers.

All computer work was done at the Oklahoma State University Computer Center. Initial calculations were made using an IBM 1410, and the work was completed on an IBM 7040.

Preparation of Solutions

H₂Ch-Hf Containing No Fluoride.

In the process of deciding what concentrations of Hf and H$_2$Ch were to be used in this work, several solutions of various concentrations were prepared and scanned on the Beckman DK-1 from 380 to 240 mμ using 1 cm silica cells with 3M perchloric acid as a reference. It was found that H$_2$Ch solutions of over 1.00 x 10^{-4}M gave absorbances of over 2.00 at the absorption maximum of about 300 mμ. Solutions containing up to 1.00 x 10^{-3}M Hf were also scanned but no apparent absorption occurred in the range from 380 to 240 mμ. Several other solutions containing both 10^{-4}M H$_2$CH and 10^{-3}M Hf were run but none gave absorption values of over 2.00 between 380 and 240 mμ. It was decided, therefore, to restrict concentrations of H$_2$Ch and Hf to 1.00 x 10^{-4} and less.

Two series of solutions were then made up in 3M perchloric acid, one containing H$_2$CH only at various concentration levels and the other series containing both Hf and H$_2$Ch. The first series of twelve solutions containing H$_2$Ch only was prepared using 1.00 x 10^{-4} molar H$_2$Ch which was made up by diluting 25 ml of the 1.00 x 10^{-3} stock to exactly 250 ml in a Pyrex volumetric flask. The solutions were prepared by using a 25 ml precision buret to introduce 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 22, and 24 ml of 1.00 x 10^{-4}M H$_2$Ch into 25 ml Pyrex volumetric flasks. The flasks were then filled to the mark with 3M perchloric acid. This procedure gave solutions in which the concentration of H$_2$Ch ranged from 0.08 to 0.96 x 10^{-4} molar in steps of 0.08 x 10^{-4}M.

The second series of solutions containing H$_2$CH and Hf was made up in exactly the same manner except 1.00 x 10^{-4}M Hf in 3M perchloric acid

was used to make the dilutions in the 25 ml volumetric flasks instead of just 3M perchloric acid. The 1.00×10^{-4}M Hf in 3M perchloric acid was prepared by diluting 25 ml of the previously mentioned 1.00×10^{-3}M stock solution of Hf to 250 ml with 3M perchloric acid. This procedure of make-up gave a series of 12 solutions in which the total molar concentration of Hf plus H_2CH was 1.00×10^{-4}M and the molar concentration ratio of H_2CH to Hf ranged from 0.087:1 to 24:1. As noted above, in both series of solutions, the total H_2Ch concentration was the same for corresponding solutions, namely from 0.08 to 0.96×10^{-4}M in steps of 0.08×10^{-4}. The stoichiometry of all twenty-four solutions is given in Table I.

H_2Ch-Hf Containing Fluoride.

After interpretation and evaluation of the results of the preceding section it was decided to approach the fluoride masking effect in much the same manner. In order to facilitate comparison of the data, the solutions investigated should have the same stoichiometry except for the presence of F^-.

In order to effectively see the masking effect of F^-, that is, the exchange of chloranilate for F^-, the ratio of H_2Ch to Hf must be sufficiently high for formation of higher ordered H_2Ch-Hf complexes. In view of this, it was decided to study two of the solutions described in the previous section, namely, the 4:1 and 7.33:1 H_2Ch to Hf solutions.

Volumetric ware resistant to fluoride was required for make-up of fluoride solutions. A 50 ml volumetric tube consisting of a 50 ml Nalgene centrifuge tube fitted with a narrow tubular neck had been constructed by a fellow graduate student. The tube was recalibrated at

TABLE I

STOICHIOMETRY OF 1.00×10^{-4} M H_2Ch-Hf SOLUTIONS AND H_2Ch SOLUTIONS
IN 3M PERCHLORIC ACID IN THE ABSENCE OF FLUORIDE

Milliliters of 1.00×10^{-4} M stock added to each 25 ml volumetric flask		1.00×10^{-4} M H_2Ch Plus Hf			H_2Ch Without Hf
H_2CH	Hf	Molarity of $H_2Ch \times 10^{-4}$	Molarity of Hf $\times 10^{-4}$	Molar Ratio H_2Ch: Hf	Molarity of $H_2Ch \times 10^{-4}$
2	23	.08	.92	.087	.08
4	21	.16	.84	.190	.16
6	19	.24	.76	.316	.24
8	17	.32	.68	.471	.32
10	15	.40	.60	.667	.40
12	13	.48	.52	.923	.48
14	11	.56	.44	1.28	.56
16	9	.64	.36	1.79	.64
18	7	.72	.28	2.59	.72
20	5	.80	.20	4.00	.80
22	3	.88	.12	7.33	.88
24	1	.96	.04	24.0	.96

exactly 50.00 ml using distilled water and used throughout the F⁻ work. Periodic checking of the calibration proved the tube to be highly reliable, ± 0.07 ml.

4:1 H_2Ch:Hf Solutions Containing F⁻. Since the volume of each sample was set at 50.00 ml, it was decided to pipet 10.00 ml of H_2Ch and 10.00 ml of Hf solution into the 50 ml Nalgene volumetric tube, add the appropriate amount of hydrofluoric acid and dilute to volume with 3M perchloric acid.

For a 4:1 molar ratio of H_2Ch to Hf at a total concentration of H_2Ch plus Hf of 1.00×10^{-4}M the concentration of H_2Ch was 0.80×10^{-4}M and Hf 0.20×10^{-4}M. In order to pipet 10.00 ml of each H_2Ch and Hf the molarity of each stock solution had to be 4.00×10^{-4} and 1.00×10^{-4} respectively. The H_2Ch stock solution was prepared from the original stock solution of 1.00×10^{-3}M by pipetting 200 ml into a 500 ml volumetric flask and diluting to the mark with 3.00M perchloric acid, thus giving the desired 4.00×10^{-4}M H_2Ch in 3M perchloric acid. The Hf stock solution was prepared by pipetting 20.00 mls of the original 1.00 $\times 10^{-3}$M stock into a 200 ml volumetric flask and diluting to the mark with 3.00M perchloric acid giving the desired 1.00×10^{-4}M Hf in 3.00M perchloric acid.

The fluoride ion concentration range used in this study was from zero to an experimental limit of about 2.00×10^{-4}M. This choice was based upon previous work (13) (11) and some unpublished work by Nicolson (7), in 1962. After the addition of the 10 ml of 4.00×10^{-4}M H_2Ch and 1.00×10^{-4}M Hf to the 50.00 ml volumetric tube the appropriate amount of hydrofluoric acid was added before addition of the 3.00M perchloric acid to the mark.

In order to determine the amount of hydrofluoric acid to be added to each solution the following calculations were necessary. Based on the work of Caglioti (3), Varga and Hume (9) had given the stepwise dissociation constants for the HF system as follows:

$$HF = H^+ + F^- \quad Ka = 5.37 \times 10^{-4}$$

$$HF_2^- = HF + F^- \quad Ka_2 = 8.1 \times 10^{-2}$$
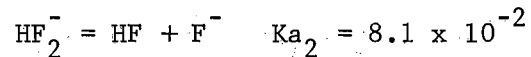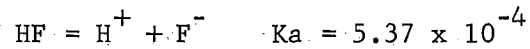
where:

$$Ka = \frac{[H^+][F^-]}{[HF]} \quad \text{and} \quad Ka_2 = \frac{[HF][F^-]}{[HF_2^-]}$$

At low HF concentrations, below 0.2M, the free hydrogen ion concentration $[H^+]$ was taken as 3.00M. The fluoride ion concentration was calculated according to the following equation given by Varga (12):

$$(1) \qquad [F^-] = \frac{C_A}{\dfrac{[H^+]}{Ka} + 1 + \dfrac{2}{Ka_2}(C_H - [H^+])}$$

where C_A = total F^- concentration = $[HF] + 2[HF_2^-] + [F^-]$

C_H = total H^+ concentration = $[H^+] + [HF] + [HF_2^-]$

At low fluoride as stated above $C_H - [H^+]$ can be considered equal to C_A which reduces equation 1 above to the following:

$$(2) \qquad [F^-] = \frac{C_A}{\dfrac{[H^+]}{Ka} + 1 + \dfrac{2}{Ka_2}(C_A)}$$

In this work it was desired to have a selected F^- concentration, therefore a calculation of C_A was necessary. Rearrangement of 2 gave the following which was used in calculating C_A in all F^- containing solutions except where the $[F^-]$ was above 5.00×10^{-5}M.

(3)
$$C_A = \frac{[F^-]\frac{[H^+]}{Ka} + 1}{1 - \frac{2[F^-]}{Ka_2}}$$

Where the $[F^-]$ was above 5.00×10^{-5} (C_A above 0.2M) another equation given by Varga (12) was used.

(4)
$$\frac{2[H^+]}{KaKa_2}[F^-]^2 + \left[\frac{[H^+]}{Ka} + 1\right][F^-] - C_A = 0.$$

This equation can be developed knowing the following:

$$C_A = [HF] + 2[HF_2^-] + [F^-]$$

$$\frac{[H^+][F^-]}{[HF]} = Ka \text{ and } \frac{[HF][F^-]}{[HF_2^-]} = Ka_2.$$

When C_A exceeds 0.2M, $[H^+]$ cannot be considered 3.00M just from the 3M perchloric acid solvent because of the contribution of $[H^+]$ from the HF present. Thus to solve equation 4, which contains 3 unknowns, some method had to be developed to evaluate the hydrogen ion concentration $[H^+]$ since the F^- concentration was set for convenience and C_A was to be calculated.

For the evaluation of the hydrogen ion concentrations of 3.00M perchloric acid solutions containing more than 0.2M HF a plot of log C_A versus $[H^+]$ was made of data obtained by Nicolson referenced above. These data had been obtained by measuring the $[H^+]$ potentiometrically at various levels of C_A in 3M perchloric acid solvent. The $[H^+]$ for this work was then evaluated from the experimental curve. This graph and the data of Nicolson are given in Figure 1.

After evaluation and calculation of the C_A and $[H^+]$ for the various levels of fluoride given in Table II solutions of HF in water were made
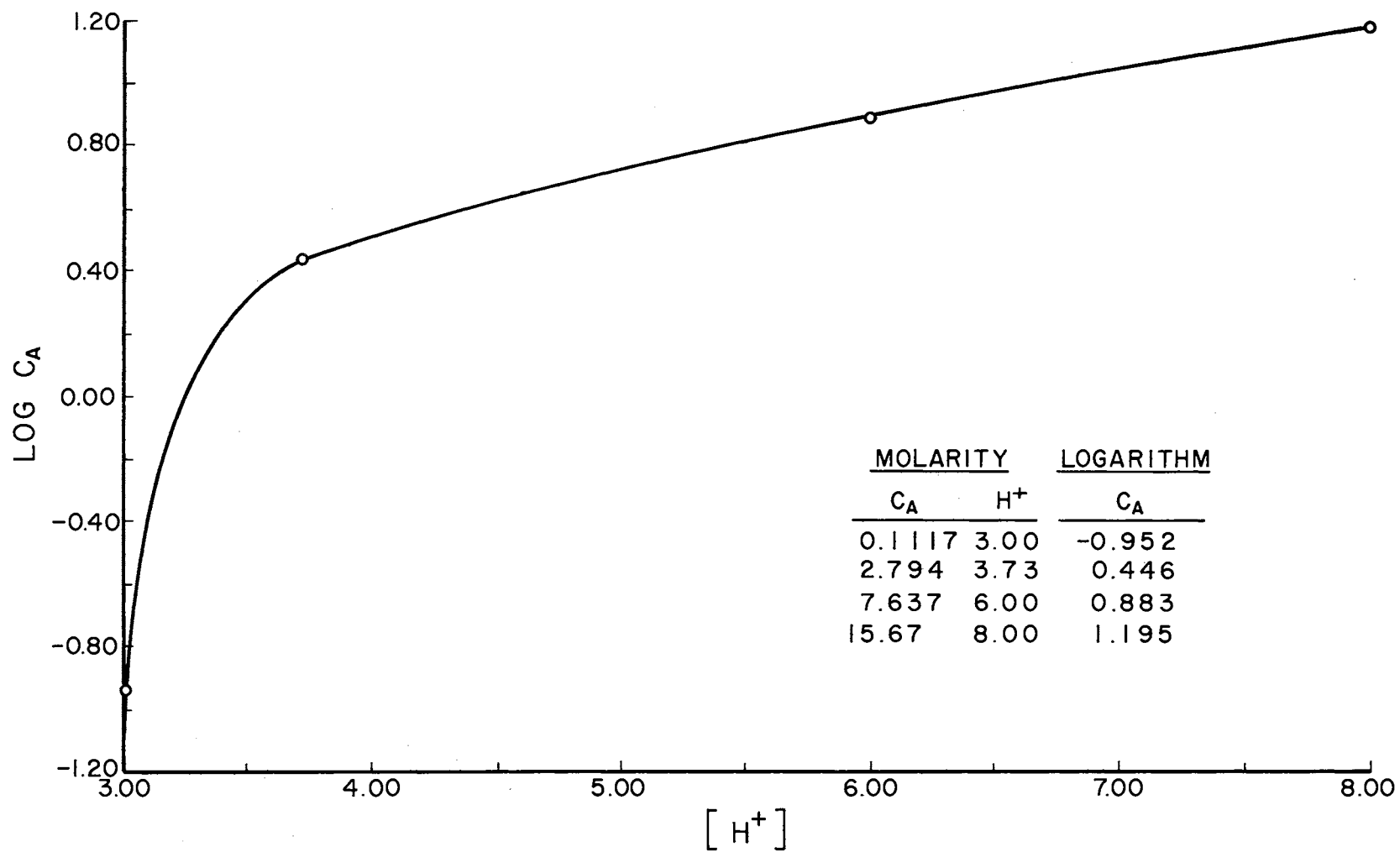
Figure 1. Plot of Log C_A vs. Hydrogen Ion Concentration

MOLARITY		LOGARITHM
C_A	H^+	C_A
0.1117	3.00	-0.952
2.794	3.73	0.446
7.637	6.00	0.883
15.67	8.00	1.195

up to facilitate addition of small amounts to the volumetric tube containing the H_2Ch and Hf. These amounts were necessarily kept small so as to prevent the $[H^+]$ from being changed by dilution. To facilitate addition of HF solutions, calibrated plastic or Nalgene Mohr pipets were used. In cases where more than 2 ml were added a polystyrene buret was used.

The HF solutions were prepared using the 48.7% HF described earlier. One liter of approximately 10M HF was made up using 330 ml of concentrated HF and diluting to one liter with deionized water. This solution was then standardized against 1.184M sodium hydroxide which had been standardized against potassium acid phthalate. After standardization of the 10.16M HF, one hundred ml of this solution was diluted with deionized water to 1 liter. This solution was standardized and the process of dilution and standardization repeated until five solutions of HF were obtained with the following molarities: 10.16, 0.9398, 0.0997, 0.0102 and 0.00106. The various amounts of HF needed in each $Hf-H_2Ch$ solution were then calculated as described above and added to the $Hf-H_2Ch$ solutions as shown in Table II. Twelve solutions were prepared with the $[F^-]$ ranging from 0.0 to 1.83×10^{-4}M and the H_2Ch:Hf molar ratio 4:1 in all twelve solutions.

Since it was expected that fluoride ion would have little or no effect on solutions containing just H_2Ch, only five solutions were prepared containing no Hf. These solutions were made up exactly as the 12 solutions containing Hf but the 10 ml of 1.00×10^{-4}M Hf was omitted. These solutions contained fluoride concentrations ranging from 0.0 to 1.83×10^{-4}M as shown in Table II.

7.33:1 H_2Ch:Hf Solutions Containing Fluoride.

In the preparation of the 7.33:1 H_2Ch:Hf at a total concentration of H_2Ch plus Hf equal to 1.00×10^{-4}M, the same concentrations of stock

TABLE II

STOICHIOMETRY OF 1.00×10^{-4} M 4:1 H_2Ch-Hf SOLUTIONS AND 0.80×10^{-4} M H_2Ch SOLUTIONS IN 3M PERCHLORATE ACID IN THE PRESENCE OF FLUORIDE

Volume and Molarity of HF Added to 50.00 ml Calibrated Tube		1.00×10^{-4} M 4:1 H_2Ch-Hf Containing 0.80×10^{-4} M H_2Ch Plus 0.2×10^{-4} M Hf			0.80×10^{-4} M H_2Ch
1.00×10^{-4} M 4:1 H_2Ch:Hf	0.80×10^{-4} M H_2Ch	$[H^+]$	Molarity of HF	Molarity of F^-	Molarity of F^-
0	0	3.00	0	0	0
0.264 ml 0.00106M	0.264 ml 0.00106M	3.00	5.59×10^{-6}	1.00×10^{-9}	1.00×10^{-9}
2.64 ml 0.00106M	-	3.00	5.59×10^{-5}	1.00×10^{-8}	-
2.74 ml 0.0102M	-	3.00	5.59×10^{-4}	1.00×10^{-7}	-
2.80 ml 0.0997M	-	3.00	5.59×10^{-3}	1.00×10^{-6}	-
5.60 ml 0.0997M	-	3.00	1.12×10^{-2}	2.00×10^{-6}	-
1.48 ml 0.9398M	1.48 ml 0.9398M	3.00	2.80×10^{-2}	5.00×10^{-6}	5.00×10^{-6}
2.97 ml 0.9398M	-	3.00	5.59×10^{-2}	1.00×10^{-5}	-
5.94 ml 0.9398M	-	3.00	1.12×10^{-1}	2.00×10^{-5}	-
1.38 ml 10.16M	-	3.06	2.80×10^{-1}	4.91×10^{-5}	-
2.76 ml 10.16M	2.76 ml 10.16M	3.14	5.60×10^{-1}	9.56×10^{-5}	9.56×10^{-5}
5.51 ml 10.16M	5.51 ml 10.16M	3.28	1.12	1.83×10^{-4}	1.83×10^{-4}

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solutions used in the 4:1 preparation were used, namely 1.00×10^{-3}M H_2Ch and Hf. From the 1.00×10^{-3}M H_2Ch, a 4.00×10^{-4}M stock solution of H_2Ch was prepared as described in the 4:1 make-up. A 2.00×10^{-4}M stock solution of Hf was prepared using 40 ml of 1.00×10^{-3}M Hf diluted to 200 ml.

For a 7.33:1 ratio of H_2Ch:Hf the molarity of the H_2Ch had to be 0.88×10^{-4} and that of the Hf 0.12×10^{-4} giving the desired H_2Ch plus Hf molarity of 1.00×10^{-4}. Since the volume of each solution to be prepared was 50.00 ml, 11 ml of 4.00×10^{-4}M H_2Ch and 3 ml of 2.00×10^{-4}M Hf were required to give the desired concentrations. Therefore, 11 ml of 4.00×10^{-4}M H_2Ch were added to the 50.00 ml volumetric tube using a precision 25 ml buret and three ml. of the 2.00×10^{-4}M Hf were added using a pipet. The HF concentrations were exactly the same as in the case of the 4:1 H_2Ch-Hf solutions, therefore these additions were made as described in the 4:1 make-up section.

The twelve solutions prepared in this manner gave a 7.33:1 molar ratio of H_2Ch:Hf at a total concentration of H_2Ch plus Hf equal to 1.00×10^{-4}M with the $[F^-]$ ranging from 0.00 to 1.83×10^{-4}M as shown in Table III.

A similar set of 2 solutions was prepared in exactly the same manner but without the 3 ml of 2.00×10^{-4}M Hf. These 2 solutions were used to determine if fluoride ion had any effect upon the H_2Ch.

The stoichiometry of all 14 solutions is given in Table III.

Procedure

Solutions With Fluoride Absent.

H_2Ch Solutions. To determine the absorption characteristics of the

TABLE III

STOICHIOMETRY OF 1.00×10^{-4}M 7.33:1 H_2Ch-Hf SOLUTIONS AND 0.88×10^{-4}M

H_2Ch SOLUTIONS IN 3M PERCHLORIC ACID IN THE PRESENCE OF FLUORIDE

Volume and Molarity of HF Added to 50.00 ml Calibrated Tube		1.00×10^{-4}M 7.33:1 H_2Ch:Hf Containing 0.88×10^{-4}M H_2Ch plus 0.12×10^{-4}M Hf			0.88×10^{-4}M H_2Ch
1.00×10^{-4}M 7.33:1 H_2Ch:Hf	0.88×10^{-4}M H_2Ch	$[H^+]$	Molarity of HF	Molarity of F^-	Molarity of F^-
0	0	3.00	0	0	0
0.264 ml 0.00106M	-	3.00	5.59×10^{-6}	1.00×10^{-9}	-
2.64 ml 0.00106M	-	3.00	5.59×10^{-5}	1.00×10^{-8}	-
2.74 ml 0.0102M	-	3.00	5.59×10^{-4}	1.00×10^{-7}	-
2.80 ml 0.0997M	-	3.00	5.59×10^{-3}	1.00×10^{-6}	-
5.60 ml 0.0997M	-	3.00	1.12×10^{-2}	2.00×10^{-6}	-
1.48 ml 0.9398M	-	3.00	2.80×10^{-2}	5.00×10^{-6}	-
2.97 ml 0.9398M	-	3.00	5.59×10^{-2}	1.00×10^{-5}	-
5.94 ml 0.9398M	-	3.00	1.12×10^{-1}	2.00×10^{-5}	-
1.38 ml 10.16M	-	3.06	2.80×10^{-1}	4.91×10^{-5}	-
2.76 ml 10.16M	-	3.14	5.60×10^{-1}	9.56×10^{-5}	-
5.51 ml 10.16M	5.51 ml 10.16M	3.28	1.12	1.83×10^{-4}	1.83×10^{-4}

H_2Ch dissolved in 3M perchloric acid, several solutions at various con-
centration levels of H_2Ch were scanned on the Beckman DK-1 recording
spectrophotometer. Three molar perchloric acid was used as the refer-
ence solution in all runs. Using 1 cm matched silica cells, scanning
was performed from 380 to 240 mμ. Previous workers (13) had shown the
absorption maximum for H_2Ch in 3M perchlorate was 302 mμ and this was
found to be the case in this work, also. A portion of the absorption
curve of 4.80 x 10^{-5}M H_2Ch is presented in Figure 2.

During the course of this preliminary work it was discovered that
solutions of H_2Ch in 3M perchloric acid were stable for only three to
four days. After this period absorption values decreased rapidly. There-
fore, all subsequent absorption measurements on all solutions were
completed within two to three days after make-up.

The absorbances of the twelve solutions of H_2Ch in 3M perchloric acid
listed in Table I were then measured as carefully as possible on a Beck-
man DU spectrophotometer using 1 cm silica cells with 3M perchloric
acid as a reference. Absorbances were measured in steps of 5 mμ from
360 to 260 mμ. This range was based upon the curves obtained on the DK-I
which indicated most of the absorbance occurred between 360 and 260. After
runs of several sets of solutions prepared identically to determine the
reproducibility of the system, the absorbance data for one of the sets
was arranged in matrix form. This was accomplished by listing the 21
wavelengths vertically from 260 upward to 360 mμ and the solution
stoichiometry horizontally from left to right on the page. The 252 ab-
sorbance values gave a 21 x 12 matrix in Table V which was used in all
interpretation of results.

H$_2$Ch Plus Hf Solutions. The absorption characteristics of several H$_2$Ch plus Hf solutions listed in Table I were measured on the DK-1 as described above for the H$_2$Ch solutions. Three molar perchloric acid was again used as a reference solution and scanning was performed from 380 to 240 mμ using matched 1 cm silica cells. The same peak at 302 mμ was observed in these solutions indicating free H$_2$Ch but a shoulder on the curve was noted at about 325 mμ. Previous work (13) had indicated a maximum for the H$_2$Ch-Hf complex should occur at 327 mμ, therefore it was desired to verify this observation. This was accomplished by measuring the absorption on the DK-1 from 360 to 260 mμ of a H$_2$Ch-Hf solution, in which Hf was 5.2 x 10^{-5}M and the free H$_2$Ch was originally 4.8 x 10^{-5}M, and the absorption of the 4.8 x 10^{-5}M H$_2$Ch solution described in the previous section. The resulting absorption values are plotted in Figure 2. The H$_2$Ch-Hf complex absorption values were then obtained by subtracting the free H$_2$Ch absorbances at every 5 mμ from the H$_2$Ch-Hf absorbances and plotting the resulting values which gives the absorption maximum at 327 mμ as shown in Figure 2.

Solution aging also occurred in the H$_2$Ch-Hf system and absorption loss of the solutions was even more apparent than in the H$_2$Ch solutions. Consequently, all measurements were made within two days of the make-up.

The absorbances of the H$_2$Ch-Hf solutions were measured on the DU from 360 to 260 mμ in 5 mμ steps in the same manner as the H$_2$Ch solutions above. One cm silica cells were used with 3M perchloric acid as a reference. Several sets were run and then the last set, which was run the same day as the last set of H$_2$Ch solutions, was used to construct a 21 x 12 matrix of absorbance values as was done for the H$_2$Ch system. This matrix is shown in Table VII.
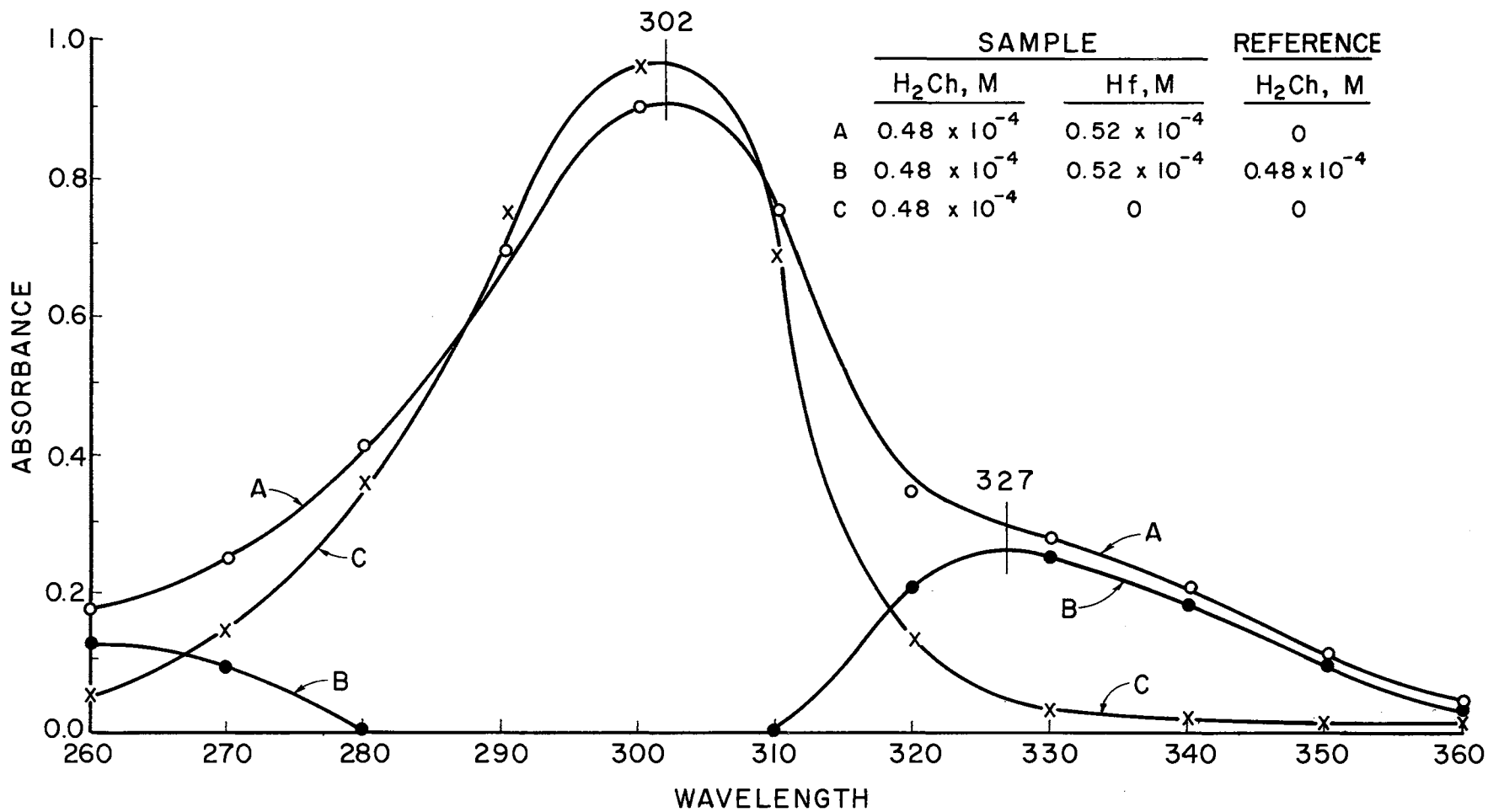
Figure 2. Spectral Scans of the H_2Ch-Hf System in 3M Perchloric Acid

Solutions With Fluoride Present.

Hf Present. The two sets, 4:1 and 7.33:1, of H_2Ch-Hf solutions containing F^- were evaluated in much the same manner as the solutions without fluoride. The absorbances were measured on the DU from 345 to 245 $m\mu$ in 5 $m\mu$ steps using silica cells and with 3M perchloric acid as a reference. The wavelength span used in this case was shifted, based upon an observation in the previous data which was indicated in the three dimensional plots. A growing peak was noted in the H_2Ch-Hf plots along the lower $m\mu$ limit of 260, therefore a shift was made in order to more closely observe the phenomenon.

The absorbance data for each of the two sets of solutions was then arranged as before in a 21 x 12 matrix. The 4:1 matrix is given in Table IX and the 7.33:1 in Table XIII.

Hf Absent. The companion sets of solutions containing no Hf were also treated in the same manner as before. However only 5 solutions of H_2Ch at 0.80 x 10^{-4} M were used. The various amounts of F^- added were not expected to affect the absorbance, therefore, the average of the absorbances of the 5 solutions at each wavelength was used to form the 21 x 12 matrix in Table XI. The resulting matrix consists of 21 rows of wavelengths and 12 columns of identical absorption values. Measurements were made as before on the DU using 3M perchloric acid as a reference, 1 cm silica cells, and from 345 to 245 $m\mu$ in 5 $m\mu$ steps.

The two solutions in which the H_2Ch concentration was 0.88 x 10^{-4} were handled exactly as above. After averaging the absorbances at each wavelength, the data were used to form the matrix in Table XV.

CHAPTER IV

COMPUTER PROGRAMS USED IN THE ANALYSIS OF DATA

Rank of a Matrix

A method for the determination of the rank of a matrix has been developed by Wallace and Katz (15) to determine the number of independent absorbing species in a series of solutions from absorption spectra. Absorption spectra are recorded for a series of solutions containing absorbing species whose relative concentrations change from one solution to the next. These absorbances as functions of wavelength and solution make-up are then arranged in a rectangular matrix and the number of components or absorbing species is determined by the rank of the matrix.

General Outlining of Rank Method

The method for the determination of the rank of the matrix consists of setting up, in addition to the absorbance matrix, A, a similar matrix, S, in which the elements, S_{ij}, are the estimated errors of the measured A_{ij}. A is then reduced by a series of elementary operations to an equivalent matrix, whose elements below the principal diagonal are all zero. The error matrix, S, is also transformed continuously during the reduction of A by computing new values of S_{ij} based on the propagation of errors in transforming A_{ij}. The rank of A is then found from the number of rows in the reduced matrix in which the absolute value of the first

element above the principal diagonal exceeds or is equal to the corresponding absolute value of the element in the reduced, S, matrix. In this work the value of the reduced matrix element, A_{ij}, on the diagonal had to be equal to or greater than three times the absolute value of S_{ij}. This requirement, that A_{ij} be at least three times its error to be called significant, is a normal criteria in spectrophotometric and other analytical calculations.

Detailed Description of Method

In performing this reduction of the matrices several elementary operations were performed. The A matrix was pivoted by an interchange of rows and columns to place the element whose absolute value was the largest in the matrix in the 1,1 position. The S matrix was at the same time transformed by the same row-column interchanges made in A. The resulting A matrix was then transformed to an A' matrix by the following operation performed on all rows except the first.

$$(1) \qquad A'_{ij} = A_{ij} - \frac{A_{i1}}{A_{11}} A_{1j}$$

By this operation all elements of the first column are zero except of course the first row. S was transformed to S' by the equation for the propagation of errors in equation 1.

$$(2) \qquad S'_{ij} = \left[S^2_{ij} + S^2_{1j} \left(\frac{A_{i1}}{A_{11}}\right)^2 + S^2_{i1} \left(\frac{A_{1j}}{A_{11}}\right)^2 + S^2_{11} \left(\frac{A_{i1}A_{1j}}{A^2_{11}}\right)^2 \right]^{\frac{1}{2}}$$

The submatrices formed by deleting the first row and column of A' and S' were then treated in the same manner to give A'' and S''. This process of deleting rows and columns was then repeated until all elements of the transformed A matrix below the principal diagonal were identically

zero. The rank was then taken as the number of rows in which the A' element was equal or greater than three times the corresponding S' element.

Fortran Program

Wallace and Katz had written a "Fortran" program for an IBM 704 computer and a copy was obtained from them for use in this work. The program was modified to fit the IBM 1410 and one change was made in the program so that, after each step in the reduction of A, each element was compared with the product of the corresponding element in S and some pre-selected criterion. If the absolute value of the element in A was less than or equal to that product, it was set identically equal to zero. This was necessary to prevent the computer from writing very small, insignificant values below the principal diagonal. This criterion was kept necessarily small to prevent an A element from being set arbitrarily equal to zero. In this work the criteria was 0.001. A listing of the computer program is presented in Appendix A.

Significance of Rank

The rank of a matrix indicates the number of absorbing species present in the system when the matrix is made up of absorbance data taken from solutions where the concentration of the absorbing species varies from solution to solution. The rank, then, is a measure of the number of independent peaks and valleys present in an array of absorbance values when these values are arranged in ordered matrix form.

As the concentrations of the absorbing species changed from one solution to the next, it was necessary to distinguish the peaks and valleys caused by significant concentrations of the species from ripples caused

by random errors in the experimental data. If no lower limit were set on

the significance of a change in the absorption spectra from one solution

to the next, the number of solutions present in the system, i.e., the

number of columns in the matrix, would be the rank of the matrix.

It was, therefore, necessary to limit the lower level of the error

in the S matrix so that the rank of the A matrix was really a measure of

the independent absorbing species and not just a measure of differences

in absorption values due to these errors in solution make-up, handling

and absorbance measurements.

Error Evaluation

Preliminary work on the computer using the H_2Ch data of Table V

gave a rank of five, indicating the presence of five independent peaks

and valleys in the twelve solutions of H_2Ch in 3M perchloric acid. Since

a rank of one was expected, indicating one species, an evaluation of the

error was deemed necessary.

The error used in the preliminary work had been ± 0.003 absorbance

units, which Wallace and Katz had used in their work. It was decided to

do an error study in which the error ranged from ± 0.002 to a limit of

± 0.050 absorbance units and observe the rank as a function of error.

A loop was inserted in the program to accomplish this and the results

of this study are given in Table IV.

As shown in Table IV the rank remained constant in the range of

error from ± 0.10 upward for the H_2Ch data of Table V. Later work is

also presented in Table IV for the H_2Ch-Hf and H_2Ch-Hf-HF systems in

which the rank was constant over the range of error from ± 0.016 to

± 0.040. This evaluation of error led to the decision that the ideal

TABLE IV

ERROR SIZE AND ITS RELATIONSHIP TO THE RANK OF AN

ABSORBPTION MATRIX

H_2Ch Matrix of Table V			H_2Ch-Hf Matrix of Table VII			H_2Ch-Hf Plus F^- matrix of Table IX	
Error	Rank		Error	Rank		Error	Rank
.003	5		.002	5		.002	5
.006	4		.004	5		.004	5
.010	1		.006	4		.006	4
.015	1		.008	4		.010	4
.020	1		.010	4		.015	3
.025	1*		.012	4		.020	3
.030	1		.014	4		.025	3*
.035	1		.016	3		.030	3
.040	1		.018	3		.035	3
.045	1		.020	3		.040	3
.050	1		.022	3		.045	2
			.024	3		.050	2
			.025	3*			
			.026	3			
			.028	3			
			.030	3			
			.035	3			
			.040	3			
			.045	2			
			.050	2		*Mean Value	

error for the systems in this thesis was ± 0.025 absorbance units which was the mean for all systems where the rank remained constant. Therefore all subsequent rank determinations were made using 0.025 as the error matrix as shown in Table V.

Rank of Experimentally Measured Absorbance Matrices

H_2Ch in 3M Perchloric Acid

The matrix of Table V for the solutions of H_2Ch in which the concentration ranged from 0.08 to 0.96 x 10^{-4}M in 3M perchloric acid was then subjected to the rank determination on the computer. The error matrix used is given in Table V also. By comparing the reduced A' and S' matrices for this system in Table VI, it can be seen that only the first value in row 1 of A' exceeds three times the corresponding value in row 1 of S'. The value of row 2 first above the diagonal does not exceed three times the value of row 2 just above the diagonal. Thus this system has a rank of one, indicating one absorbing species.

H_2Ch-Hf(IV) in 3M Perchloric Acid

The H_2Ch-Hf(IV) system in which the molar concentration of H_2Ch plus Hf^{+4} was 1.00 x 10^{-4}M and the molar ratio of H_2Ch:Hf was from 0.087:1 to 24:1 produced the matrix given in Table VII. After subjecting this matrix to machine calculations; using the same error matrix given in Table V, the reduced A' and S' were produced and are given in Table VIII. Here it can be seen, as was described above, that three rows in A' have values just above the diagonal which exceed or are equal to three times the corresponding values in S'. The rank, then, of this matrix was three.

4:1 H_2Ch:Hf Plus F^- in 3M Perchloric Acid

In this system where the H_2Ch concentration was $0.80 \times 10^{-4}M$ and the total Hf^{+4} $0.20 \times 10^{-4}M$ in all twelve solutions, only the amount of F^- varied. This produced a change in solution absorbance as the amount of H_2Ch-Hf(IV) complex was reduced by the added F^- which formed a non-absorbing complex. As the fluoride concentration increased from zero to $1.83 \times 10^{-4}M$ absorbances decreased as shown in Table IX. This system gave a rank of three as can be seen by inspection of the reduced A' and S' matrices in Table X.

$0.80 \times 10^{-4}M$ H_2Ch Plus F^- in 3M Perchloric Acid

In this system no effect was expected upon addition of fluoride, therefore only five solutions were made up and their absorbance values at each wavelength averaged to give the matrix of Table XI. The rank of this matrix was one as expected. In this case, as shown in Table XII, the reduced A' and S' matrices looked a bit different. All values below row 1 are zero in the A' and only the first column of S' is zero below row 1. This phenomena is due to all values at each of the 21 vertically listed wavelengths being the same for each solution. Therefore after the first reduction of A all values of A' are zero below the first row and the operation is terminated by the computer. Zeroing of all values below the principal diagonal in S is then prevented because of the zeros encountered in A.

7.33:1 H_2Ch:Hf Plus F^- in 3M Perchloric Acid

The matrix of Table XIII obtained from solutions where the H_2Ch concentration was $0.88 \times 10^{-4}M$, Hf(IV) $0.12 \times 10^{-4}M$ and F^- varying from zero to $1.83 \times 10^{-4}M$ gave a rank of two as is shown in Table XIV of the

reduced A' and S' matrices.

0.88 x 10^{-4}M H_2Ch Plus F⁻ in 3M Perchloric Acid
_____

In this matrix only two solutions were used to give the absorbance

values. The average of the absorbances of these two solutions at each

wavelength produced the matrix in Table XV. A rank of one was obtained

as is shown in Table XVI. The same phenomenon in the A' and S' matrices

occurred here as was described earlier in the case of the 0.80 x 10^{-4}M

H_2Ch in Table XII.

Three Dimensional Plotting Routine

In the previous section the matrix rank gave the number of absorb-

ing species or complexes in a given matrix of absorbance measurements. The

obvious course now would be to identify these species by some manner.

As was stated earlier the rank indicated the number of significant peaks

and valleys in an absorbance matrix. Then with a contour map or plot of

this matrix these valleys or peaks should be discernible.

As mentioned in the section, Review of the Literature, a computer

program for a three dimensional plot was available for use on the IBM

1410. Although initial plots were made on the 1410, all final contour

maps were plotted by the IBM 7040. The 1410 could handle only one half

of the data for each matrix at a time, therefore to avoid cumbersome maps,

the 7040 was used. All 252 points of each matrix could be plotted at

once on the larger 7040. The Fortran listing of the program for the

7040 is given in Appendix B.

The method of plotting the absorbance data for each matrix is quite

unique. The absorbance range can be chosen for any reasonable limit,

say from 0.000 to 2.000, which was used for the greater part of the matrices. This range can then be divided up into any number of smaller increments of absorbance, as long as the computer has a symbol for that increment. For this work the absorbance range was divided up into 40 increments, thereby giving an increment of 0.050 absorbance units to each symbol. The 40 symbols were arbitrarily chosen as follows from a lower limit of 0.000 to an upper limit of 2.000:

$$*, 1 \text{ thru } 9, 0, +, A \text{ thru } Z, /, \$$$

In choosing the correct symbol for a given absorbance value the computer simply selects the one whose value is closest to it. For example, an absorbance value of 0.012 might be represented by a 1, while 0.013 might be a 2.

The program output was a plot of wavelength on the vertical vs. solution stoichiometry on the horizontal vs. absorbance coming out of the page toward the observer. By drawing in the contour lines the individual peaks and valleys could be more closely observed. By observing the solution stoichiometry at the point where a peak or valley occurred, the ratio of H_2Ch to Hf(IV) could be ascertained. The contour maps then were used to find the H_2Ch:Hf complex ratios.

H_2Ch Solution Absorbances of Table V.

The absorbances of Table V for the H_2Ch solutions given in Table I are plotted in Figure 3. In this figure a very high ridge occurs along the maximum absorption peak of 302 mμ. The ridge also rises as the concentration increases to the right. The presence of one species, which was also the case in the rank calculations, was supported by the three dimensional plot of the same data.

Absorbances of Table VII for the H_2Ch-Hf System

The addition of Hf^{+4} to the solution of H_2Ch listed in Table I gave the contour map of absorbances in Figure 4. In addition to the H_2Ch characteristics of Figure 3, two other very important features are present. A very long peak centered over about 0.5×10^{-4}M H_2Ch is evident. In addition, a ridge has formed near the top of the map centered over about 0.75×10^{-4}M H_2Ch. These two features were interpreted as 1:1 and 3:1 complexes of H_2Ch with Hf(IV).

Absorbances of the H_2Ch-Hf System Minus H_2Ch Absorbances

In order to verify the above interpretations, a contour map was made in Figure 5 of just the features due to the H_2Ch-Hf(IV) complexes. This was accomplished by taking each absorbance value of the H_2Ch-Hf(IV) solutions in Table VII and subtracting the corresponding absorbance value of the H_2Ch solutions in Table V. In cases where the net absorbance was negative the computer was instructed to set this value equal to zero.

The resulting map very clearly shows the existence of two very sharp features. The large "loaf" shaped peak is centered over the solution concentration where the molar ratio is 1:1 for H_2Ch:Hf. This indicates the presence of a 1:1 complex of H_2Ch:Hf. The other obvious feature is a sharp ridge present in the upper right hand section of the map. The center of this ridge is situated at a solution stoichiometry where the H_2Ch:Hf ratio is 3:1. This indicates the presence of a 3:1 complex of H_2Ch:Hf.

4:1 H_2Ch:Hf Plus F^- Absorbances of Table IX

The effect of the presence of F^- in the 4:1 molar ratio of H_2Ch:Hf

system is shown in Figure 6 for the solutions of Table II. As mentioned earlier, F^- masks the absorbance of the H_2Ch-Hf system by replacing the chloranilate. At the lower left hand corner a gradual decrease in absorbance was apparent as the F^- concentration increased toward the right. This was interpreted as the decreasing concentration of the 1:1 complex due to F^- masking. Two other ridges can be seen in the upper part of the map. These are probably due to higher ordered complexes of Hf with chloranilic acid as the ratio of free H_2Ch to Hf increases as the F^- concentration increases. The free H_2Ch concentration increase arises from the replacement of the H_2Ch with F^- in the H_2Ch-Hf complex. This system was given a rank of 3, therefore two absorbing species besides free H_2Ch were indicated. Since other work in this laboratory (13) had shown an increase in the concentration of a higher ordered H_2Ch-Hf(IV) complex as the F^- concentration increased, it was assumed that the peaks in the upper portion of the map represented a 3:1 H_2Ch-Hf complex. At the higher H_2Ch concentrations, the possible presence of a 4:1 complex could be a contributing factor in the appearance of the two upper peaks in Figure 6. Future studies, beyond the scope of this thesis, will decide this point.

0.80×10^{-4}M H_2Ch Plus F^- Absorbances of Table XI.

Figure 7 shows a map of absorbance data obtained from the solutions of Table II where F^- ranged from zero to 1.83×10^{-4}M. As the F^- concentration was increased no effect was noted. Thus the map shows only the sharp ridge at 302 mμ, at which H_2Ch exhibited its maximum absorbance.

7.33:1 H_2Ch:Hf Plus F^- Absorbances of Table XIII

These data from the solutions of Table III where F^- ranged from zero

to 1.83×10^{-4}M indicated one other species besides H_2Ch. The dis-
appearance of this species was indicated in Figure 8 by the decreasing

absorbance in the lower left hand corner. This feature was the only

obvious one in the map and it was interpreted as the 1:1 complex of

H_2Ch:Hf.

0.88×10^{-4}M H_2Ch Plus F^- Absorbances of Table XV

As in the case of 0.80×10^{-4}M H_2Ch this map in Figure 9 simply shows

the absorbance maximum of H_2Ch at 302 mμ. These data were taken from the

solutions of Table III in which fluoride concentrations were zero and

1.83×10^{-4}M.

Job Plots of H_2Ch-Hf and H_2Ch Data

Other work in this laboratory (13) had used the continuous varia-

tion method of Job (6) to determine the H_2Ch:Hf ratios of the complex.

The data of Tables IV and VII were used to prepare Job plots for compari-

son with the earlier work.

The Job plots used consisted of plots of $A - (X/10) \cdot A_{X = 10}$ vs.

$(X/10)$ where

$\qquad$ A $\qquad$ = Absorbance of H_2Ch-Hf solutions at a given wavelength.

$\qquad$ $A_{X = 10}$ = Absorbance of H_2Ch solutions at a mole fraction of one at

$\qquad\qquad$ the same wavelength.

$\qquad$ $(X/10)$ = Mole fraction of H_2Ch in the H_2Ch-Hf solutions.

In order to determine $A_{X = 10}$ a calculation was done at each of the 21

wavelengths by the following equation:

$$A_{X = 10} = (\frac{1.00}{0.96}) \cdot A \text{ of } H_2\text{Ch at } 0.96 \times 10^{-4}\text{M}$$

where:

$\frac{1.00}{0.96}$ · A of H_2Ch at $0.96 \times 10^{-4}M$ gives the absorbance values of a $1.00 \times 10^{-4}M$ H_2Ch solution at each of the 21 wavelengths from 260 to 360 mμ in steps of 5 mμ. A values for this calculation are given in the last column of the H_2Ch matrix of Table V.

A Fortran program was written for the IBM 1410 which computed and plotted the Job curves. Interpretation of the 21 resulting curves was then possible by observation of the minimums and maximums and the corresponding mole fractions of H_2Ch. Five of the resulting curves are given in Figure 10 for 265, 285, 305, 325, and 345 mμ.

A maximum occurred at a mole fraction of about 0.5 in the 325 and 345 mμ curves indicating a 1:1 complex of H_2Ch:Hf. The occurrence of a minimum at 0.5 mole fraction in the 305 mμ curve was also interpreted as caused by a 1:1 complex.

At 265 and 285 mμ the curves showed a maximum at about 0.75 mole fraction of H_2Ch. Although these curves are somewhat abnormal for Job plots, it was assumed tentatively that the maximums were due to a 3:1 complex of H_2Ch to Hf.

Since this abnormality was observed and since the Job method was designed primarily for a 1:1 complex in a simple system no further interpretations based on this method were made.

Iterative Machine Calculation of β_1 and β_3

An iterative program was written for the IBM 1410. With this program a machine calculation of the formation constants, β_1 and β_3, for the 1:1 and 3:1 chloranilic acid: hafnium complexes were completed using the data and some preliminary calculations of the author.

For the calculations to be completed several known quantities were read into the computer as shown in the flowsheet of Appendix C. These values are defined as follows:

$Ab(21,12)$ = The 252 absorbance values for the 12 H_2Ch-Hf solutions at the 21 wavelengths given in Table VII.

$MA_3(12)$ = The estimated concentrations of the 3:1 complex in each of the 12 solutions.

$Ab_4(12)$ = The absorbance values of the fourth solution in Table VII where no interference of a 3:1 complex was assumed.

$C_A(12)$ = The total concentration of H_2Ch in each of the 12 solutions.

$C_M(12)$ = The total concentration of Hf in each of the 12 solutions.

$\epsilon_A(12)$ = The molar absorptivity of the H_2Ch at each of the 21 wavelengths calculated from the data of Table V.

With the data read in calculations of A(12) were made, where A(12) was the concentration of free H_2Ch in each of the 12 solutions of H_2Ch-Hf. Knowing these values $\bar{n}(12)$, the average ligand number for each of the solutions, was calculated. A value for MA, the concentration of the 1:1 complex, was then calculated for the fourth solution in Table VII knowing $\bar{n}_4$ and CM_4.

The next calculation in the program produced a value for ϵ_1, where ϵ_1 was the molar absorptivity of the 1:1 complex of solution 4 at the first

wavelength. A value for ϵ_M, the molar absorptivity of the metal in the first solution at the first wavelength, was then determined.

With the previous calculations and data available the program then entered its first iteration. In this loop values of MA, MA_3 and M, the free Hf concentration, were calculated and used to calculate the first estimate of β_1 and β_3. These values in turn were used to calculate a value of ϵ_3 which in turn was used for calculations of better values of $\bar{n}$ and MA_3. At that point the computer returned to the beginning of the loop. After 25 iterations the first values for M, MA, MA_3, $\beta_,$, β_3, $\bar{n}$ and ϵ_3 for the first solution and first wavelength were ready for printout. This same loop was then repeated for the remaining eleven solutions and printout for the first wavelength (360 mμ) was completed. At that point the average values of ϵ_3, β_1 and β_3 for the first wavelength were also computed and printed out.

The computer was then instructed to return to the first calculation of ϵ_1 and compute all the values stated above for the next wavelength. This loop, with its loops within loops, was completed for all 21 wavelengths from 360 to 260 mμ in steps of 5 mμ.

After completion of the wavelength loop the 21 values of β_1 and β_3 were averaged to give a grand average value for β_1 and β_3. These values and the reactions they represent were as follows:

$$Hf^{+4} + H_2Ch \rightleftarrows Hf(H_2Ch) \quad \beta_1 = 5.77 \times 10^3$$

$$Hf^{+4} + 3H_2Ch \rightleftarrows Hf(H_2Ch)_3 \quad \beta_3 = 8.50 \times 10^{11}$$
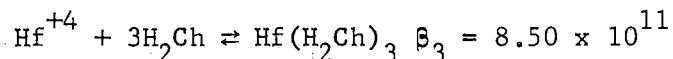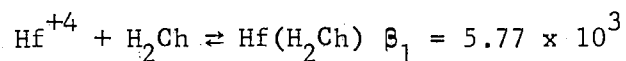
Varga, Zumwalt and Wyatt (13) had reported values for β_2 and β_4 of 4.06×10^7 and 3.10×10^{14} respectively. The values calculated by the method above and the species they represent are preferred over the previous results.

CHAPTER V

INTERPRETATION OF RESULTS

Summary and Conclusions

The matrix rank analysis of the spectrophotometric data provided a very concise method by which the number of absorbing components in a system could be determined. In the systems where fluoride was absent one component was present in the H_2Ch system and three in the H_2Ch-Hf solutions. Thus two absorbing H_2Ch-Hf complexes were found. In the fluoride containing systems one absorbing species, H_2Ch, was found in the two sets of solutions containing no Hf. Where Hf was present three absorbing species were found in the 4:1 $H_2Ch:Hf$ solutions and two in the 7.33:1 $H_2Ch:Hf$. Thus in the 4:1 solutions two complexes of H_2Ch-Hf were present and in the 7.33:1 solutions only one H_2Ch-Hf complex could be found.

Contour maps of the absorption matrices provided a very simple method for the identification of the complexes found above.

In the absence of F^- the two complexes were identified as the 1:1 and 3:1 $H_2Ch:Hf$. This was shown very clearly in Figure 5. The Job plots of this same data also indicated the existance of a 1:1 and 3:1 complex of $H_2Ch:Hf$ although some reservation was made in this interpretation.

In the presence of F^- the contour maps indicated a decreasing concentration of the 1:1 complex of $H_2Ch:Hf$ in both sets of data. In the

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case of the 4:1 $H_2Ch:Hf$ solutions, some evidence was shown for the formation of a higher complex at the expense of the 3:1 complex as fluoride was added, but this was not observed in the 7.33:1 series. No explanation was put forth and work beyond the scope of this thesis was indicated.

The iterative calculations of the formation constants for the two complexes found by the above methods gave:

For the 1:1 $H_2Ch:Hf$,

$$\beta_1 = 5.77 \times 10^3$$

For the 3:1 $H_2Ch:Hf$,

$$\beta_3 = 8.50 \times 10^{11}$$

Suggestions for Future Study

In view of the success of the computer applications presented in this thesis many more complex systems, which have resisted other means of interpretation, might well be approached in this manner. The only requirement for this approach is the collection of good, detailed data in large amounts.

The fluoride masking effect should be studied in greater detail then was presented here. The possibility of higher ordered $H_2Ch:Hf$ complexes and even mixed F^- and H_2Ch complexes of Hf should provide incentive for future work in this area. Varga, Zumwalt and Wyatt (13) had calculated the formation constants and the concentrations of complexes at one wavelength. If this were done for many more wavelengths using the data given in this thesis or new data, a more complete interpretation of the $Hf-H_2Ch-F^-$ system should be possible.

TABLE V

H$_2$Ch ABSORBANCE MATRIX FOR SOLUTIONS OF TABLE I

360	.007000000	.007000000	.008000000	.009000000	.012000000	.012000000	.012000000	.012000000	.031000000	.023000000	.031000000	.027000000
355	.007000000	.007000000	.008000000	.010000000	.012000000	.012000000	.012000000	.014000000	.032000000	.024000000	.037000000	.029000000
350	.007000000	.007000000	.009000000	.011000000	.012000000	.012000000	.012000000	.016000000	.033000000	.025000000	.038000000	.031000000
345	.007000000	.007000000	.010000000	.012000000	.013000000	.013000000	.013000000	.018000000	.037000000	.027000000	.038000000	.032000000
340	.007000000	.007000000	.011000000	.012000000	.014000000	.017000000	.017000000	.021000000	.042000000	.032000000	.046000000	.037000000
335	.007000000	.008000000	.013000000	.017000000	.018000000	.017000000	.020000000	.023000000	.048000000	.037000000	.054000000	.045000000
330	.008000000	.010000000	.018000000	.022000000	.026000000	.028000000	.030000000	.037000000	.064000000	.053000000	.073000000	.061000000
325	.013000000	.016000000	.032000000	.038000000	.049000000	.056000000	.062000000	.075000000	.107000000	.101000000	.123000000	.122000000
320	.027000000	.048000000	.073000000	.096000000	.117000000	.136000000	.158000000	.182000000	.230000000	.237000000	.275000000	.284000000
315	.062000000	.114000000	.173000000	.232000000	.288000000	.342000000	.398000000	.452000000	.544000000	.574000000	.650000000	.688000000
310	.114000000	.231000000	.343000000	.456000000	.571000000	.678000000	.792000000	.895000000	1.047000000	1.133000000	1.272000000	1.348000000
305	.158000000	.317000000	.473000000	.627000000	.782000000	.935000000	1.098000000	1.237000000	1.430000000	1.536000000	1.734000000	1.808000000
300	.163000000	.324000000	.487000000	.642000000	.803000000	.960000000	1.180000000	1.273000000	1.464000000	1.573000000	1.757000000	1.893000000
295	.146000000	.288000000	.438000000	.572000000	.725000000	.860000000	1.005000000	1.132000000	1.332000000	1.414000000	1.598000000	1.723000000
290	.122000000	.239000000	.361000000	.482000000	.603000000	.720000000	.835000000	.962000000	1.127000000	1.218000000	1.351000000	1.436000000
285	.091000000	.177000000	.270000000	.358000000	.448000000	.528000000	.614000000	.700000000	.845000000	.900000000	1.018000000	1.072000000
280	.062000000	.118000000	.183000000	.222000000	.308000000	.359000000	.422000000	.478000000	.593000000	.618000000	.712000000	.740000000
275	.039000000	.078000000	.116000000	.158000000	.198000000	.222000000	.264000000	.306000000	.404000000	.405000000	.474000000	.465000000
270	.026000000	.043000000	.071000000	.097000000	.123000000	.137000000	.158000000	.185000000	.269000000	.254000000	.315000000	.304000000
265	.014000000	.024000000	.043000000	.058000000	.075000000	.077000000	.088000000	.107000000	.186000000	.156000000	.208000000	.183000000
260	.011000000	.012000000	.026000000	.034000000	.040000000	.044000000	.048000000	.063000000	.138000000	.098000000	.148000000	.117000000

S ERROR MATRIX

.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
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.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
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.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000

TABLE VI

REDUCED H$_2$Ch MATRIX

```
1.893000000 1.757000000 1.118000000 1.573000000  .642000000 1.464000000 1.273000000  .324000000  .960000000  .803000000  .163000000  .487000000
 .000000000  .055893292  .030200740  .033631274  .013827258  .031736926  .021160592  .007548336  .018106180  .015056524  .002319070  .007867406
 .000000000  .000000000 -.042391868 -.022932480 -.015428321  .025139992 -.030598444 -.013347059 -.028099550 -.020245846 -.000709468 -.009646494
 .000000000  .000000000  .000000000  .026210945 -.001166185 -.007471704  .005983268 -.002020462  .001062242 -.000093847 -.002019539 -.005773631
 .000000000  .000000000  .000000000  .000000000 -.024615895 -.009588792 -.009274947 -.002772188 -.005585418  .001007227 -.002018441 -.003641723
 .000000000  .000000000  .000000000  .000000000  .000000000 -.013873939 -.010132383  .003015311 -.002440022  .000936915 -.001984805 -.001267875
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.007188360 -.004338185 -.002011284 -.000683742 -.001289638 -.002875165
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 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.007474612  .003287276 -.005863881 -.001972114
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```

REDUCED S MATRIX

```
 .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000
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 .000000000  .000000000  .048075669  .053739934  .038743533  .051817228  .045822148  .036037134  .042120650  .040077420  .035133979  .036705764
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 .000000000  .000000000  .000000000  .000000000  .000000000  .068952237  .066219245  .042890236  .058143686  .050001410  .038526832  .044334734
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 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .058087449  .000000000  .000000000  .120878772
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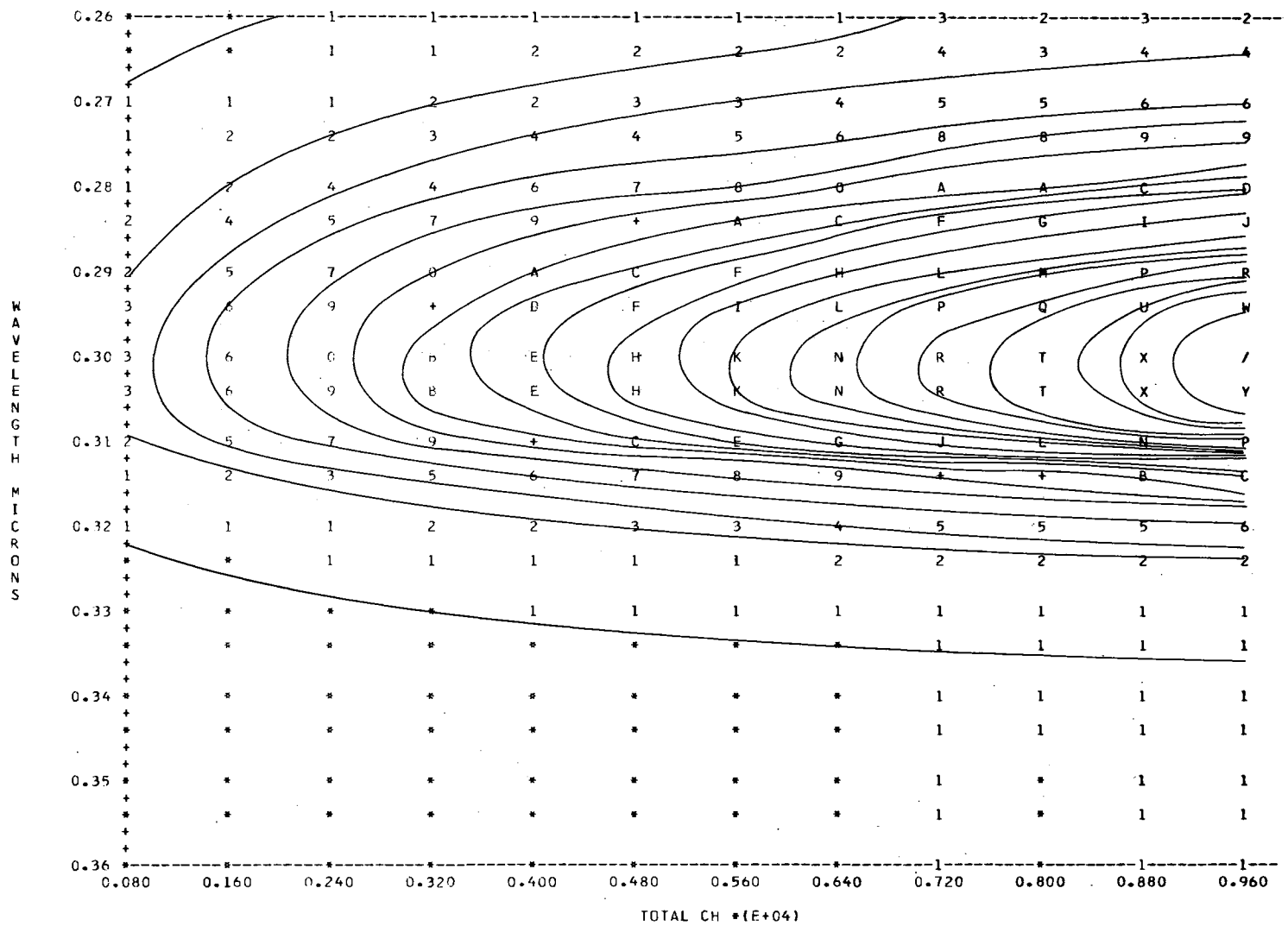
Figure 3. Contour Map of the H_2Ch Absorbance of Table V

TABLE VII

H$_2$Ch-Hf ABSORBANCE MATRIX FOR SOLUTIONS OF TABLE I

360	.020000000	.024000000	.034000000	.038000000	.042000000	.042000000	.043000000	.038000000	.037000000	.032000000	.022000000	.018000000
355	.028000000	.041000000	.051000000	.062000000	.067000000	.068000000	.069000000	.066000000	.062000000	.053000000	.037000000	.027000000
350	.038000000	.062000000	.081000000	.092000000	.103000000	.109000000	.107000000	.098000000	.093000000	.076000000	.055000000	.032000000
345	.053000000	.088000000	.114000000	.136000000	.145000000	.154000000	.150000000	.143000000	.128000000	.105000000	.075000000	.040000000
340	.066000000	.116000000	.152000000	.177000000	.196000000	.203000000	.201000000	.188000000	.169000000	.138000000	.100000000	.053000000
335	.080000000	.138000000	.182000000	.214000000	.225000000	.248000000	.242000000	.228000000	.203000000	.167000000	.118000000	.066000000
330	.087000000	.152000000	.200000000	.241000000	.266000000	.279000000	.275000000	.258000000	.234000000	.194000000	.143000000	.087000000
325	.087000000	.157000000	.212000000	.255000000	.284000000	.303000000	.301000000	.294000000	.273000000	.238000000	.192000000	.136000000
320	.090000000	.162000000	.207000000	.272000000	.317000000	.338000000	.353000000	.362000000	.357000000	.345000000	.317000000	.286000000
315	.096000000	.178000000	.252000000	.321000000	.388000000	.443000000	.494000000	.541000000	.582000000	.613000000	.625000000	.670000000
310	.108000000	.211000000	.313000000	.417000000	.516000000	.620000000	.737000000	.845000000	.960000000	1.056000000	1.166000000	1.287000000
305	.118000000	.232000000	.353000000	.476000000	.616000000	.765000000	.915000000	1.067000000	1.242000000	1.409000000	1.580000000	1.726000000
300	.114000000	.223000000	.338000000	.464000000	.607000000	.747000000	.900000000	1.064000000	1.268000000	1.452000000	1.695000000	1.775000000
295	.109000000	.202000000	.302000000	.382000000	.534000000	.663000000	.803000000	.944000000	1.161000000	1.317000000	1.478000000	1.630000000
290	.112000000	.186000000	.268000000	.359000000	.459000000	.573000000	.686000000	.805000000	1.026000000	1.163000000	1.293000000	1.425000000
285	.113000000	.169000000	.231000000	.296000000	.373000000	.454000000	.538000000	.623000000	.862000000	.967000000	1.038000000	1.147000000
280	.118000000	.158000000	.202000000	.249000000	.300000000	.352000000	.406000000	.466000000	.732000000	.792000000	.820000000	.910000000
275	.127000000	.156000000	.184000000	.213000000	.249000000	.282000000	.314000000	.350000000	.633000000	.675000000	.673000000	.720000000
270	.137000000	.152000000	.168000000	.192000000	.206000000	.227000000	.248000000	.267000000	.575000000	.594000000	.564000000	.595000000
265	.137000000	.150000000	.162000000	.173000000	.191000000	.197000000	.206000000	.213000000	.533000000	.537000000	.492000000	.505000000
260	.134000000	.144000000	.154000000	.163000000	.176000000	.177000000	.182000000	.183000000	.492000000	.488000000	.441000000	.445000000

TABLE VIII

REDUCED H$_2$Ch-Hf MATRIX

1.775000000	.747000000	1.268000000	1.695000000	.464000000	1.452000000	.338000000	.607000000	.223000000	.900000000	1.140000000	1.064000000
.000000000	.245765070	.175846197	.062129577	.219448450	.126748169	.186102535	.237491831	.139913802	.232042253	.078265352	.212476619
.000000000	.000000000	.183354549	.013685739	.054852881	.131903375	.077594065	.033308305	.095394298	-.035396547	.109510786	-.076291805
.000000000	.000000000	.000000000	-.081652628	.015213677	-.026095694	.015124399	.002957535	.012738064	.007454771	.009620571	-.000666799
.000000000	.000000000	.000000000	.000000000	-.041206586	.009648818	-.010151890	-.006245421	-.007975076	-.005998780	-.004831918	-.007195663
.000000000	.000000000	.000000000	.000000000	.000000000	.013880659	-.000750087	-.003850298	.001249812	-.008214410	.005154763	-.011729526
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.013176329	.010124389	.001259205	.003549907	.000826787	.005044900
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.009884646	-.007080554	.000176561	-.005265873	.001800889
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.010579046	.001459625	.010324600	-.002056123
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.008086339	.000639746	-.005688011
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.006691044	-.001891636
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.002843083
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.002582691
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.000174446
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.001345661
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.004295587
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.002305106
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.001791717
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.002345396
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.002048822
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	-.001161726

REDUCED S MATRIX

.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
.000000000	.027203181	.030813810	.034669100	.025915802	.032393759	.025523814	.026498842	.025270376	.028112182	.025124933	.029232946
.000000000	.000000000	.037852108	.036707808	.036889625	.036662856	.034064372	.038765477	.030781478	.039547207	.027601541	.038966265
.000000000	.000000000	.000000000	.045205447	.047381434	.056075293	.046220171	.048341694	.044868750	.049380514	.043808210	.051605695
.000000000	.000000000	.000000000	.000000000	.067206587	.080867756	.065599164	.067548970	.063429456	.069201436	.061629658	.072070349
.000000000	.000000000	.000000000	.000000000	.000000000	.071396377	.058631708	.059201218	.056113189	.060567862	.053844470	.063280379
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.055617572	.059088946	.053461073	.069901292	.056810190	.082758224
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.121413963	.089449081	.119026407	.094764684	.142277010
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.117810429	.112414709	.108343206	.135965586
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.080338979	.076659452	.073882955	.092719605
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.126898673	.130835316
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.122803995
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.113896500
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.146793689	.154299192
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.240376199
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.000000000	.000000000	.000000000	.000000000	.051030659	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.136731440
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.119292815	.000000000	.155342395
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.103517769
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.073546251	.000000000	.099055339
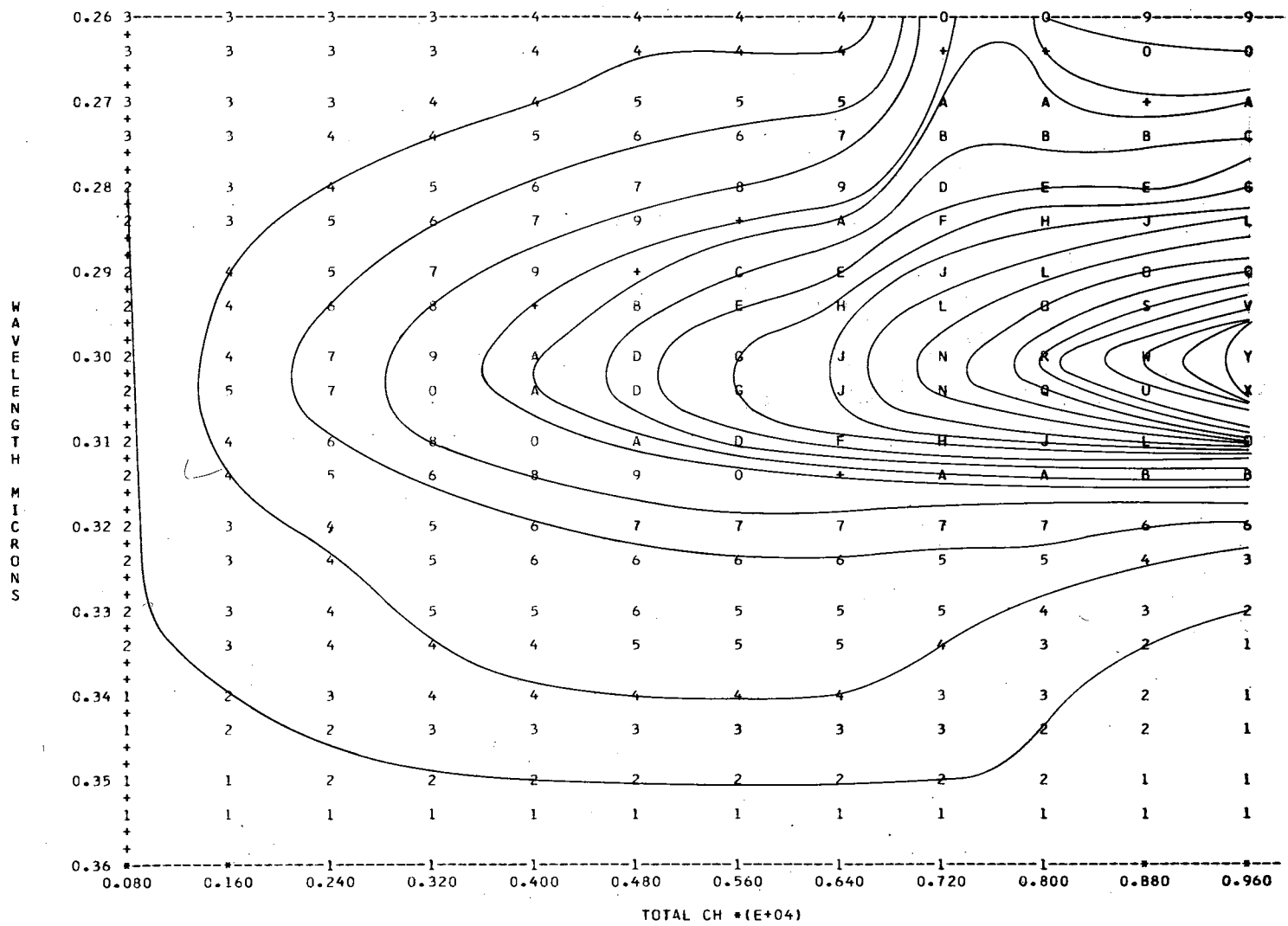
Figure 4. Contour Map of the H_2Ch-Hf Absorbances of Table VII
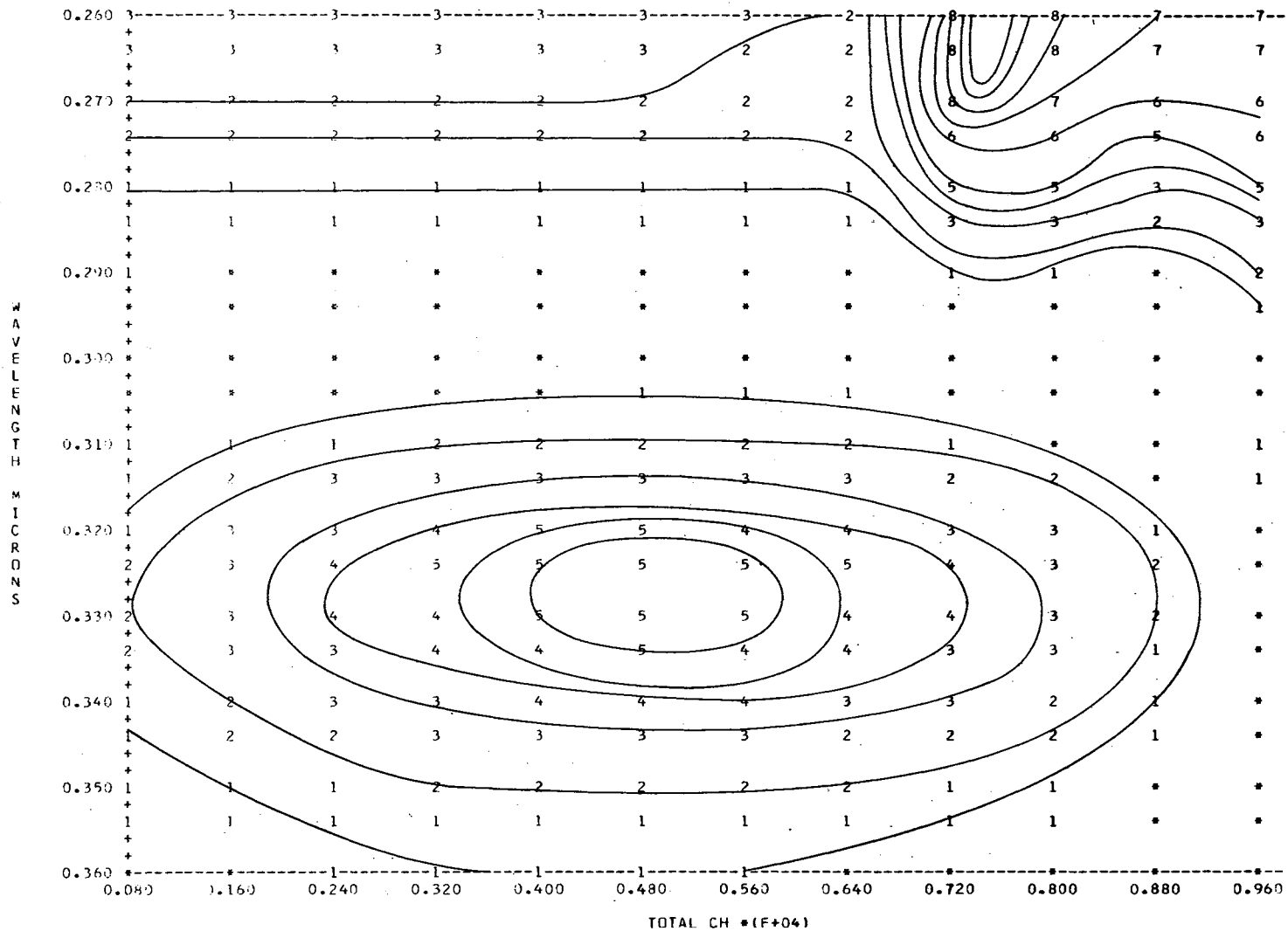
Figure 5. Contour Map of the H_2Ch-Hf Absorbances of Table VII Minus the H_2Ch

Absorbances of Table V

TABLE IX

4:1 H_2Ch:Hf PLUS F^- ABSORBANCE MATRIX FOR SOLUTIONS OF TABLE II

345	.132000000	.112000000	.076000000	.028000000	.020000000	.020000000	.018000000	.018000000	.018000000	.018000000	.017000000	.018000000
340	.176000000	.146000000	.097000000	.034000000	.023000000	.022000000	.022000000	.019000000	.022000000	.019000000	.020000000	.021000000
335	.221000000	.178000000	.120000000	.044000000	.031000000	.030000000	.028000000	.028000000	.028000000	.029000000	.027000000	.028000000
330	.245000000	.209000000	.145000000	.065000000	.048000000	.048000000	.044000000	.046000000	.048000000	.048000000	.044000000	.045000000
325	.284000000	.253000000	.192000000	.112000000	.094000000	.096000000	.093000000	.093000000	.095000000	.092000000	.092000000	.089000000
320	.384000000	.358000000	.308000000	.242000000	.227000000	.229000000	.224000000	.226000000	.231000000	.221000000	.223000000	.215000000
315	.622000000	.620000000	.598000000	.563000000	.550000000	.556000000	.548000000	.554000000	.564000000	.550000000	.553000000	.530000000
310	1.026000000	1.075000000	1.077000000	1.088000000	1.087000000	1.080000000	1.077000000	1.075000000	1.079000000	1.078000000	1.084000000	1.072000000
305	1.317000000	1.409000000	1.407000000	1.462000000	1.466000000	1.433000000	1.450000000	1.444000000	1.464000000	1.430000000	1.470000000	1.462000000
300	1.332000000	1.422000000	1.476000000	1.506000000	1.498000000	1.520000000	1.525000000	1.493000000	1.513000000	1.495000000	1.527000000	1.570000000
295	1.219000000	1.311000000	1.329000000	1.393000000	1.400000000	1.404000000	1.397000000	1.372000000	1.404000000	1.396000000	1.400000000	1.420000000
290	1.048000000	1.040000000	1.145000000	1.210000000	1.220000000	1.186000000	1.237000000	1.181000000	1.212000000	1.191000000	1.210000000	1.202000000
285	.810000000	.865000000	.895000000	.925000000	.975000000	.950000000	.945000000	.910000000	.965000000	.943000000	.960000000	.930000000
280	.600000000	.635000000	.658000000	.680000000	.740000000	.730000000	.704000000	.655000000	.732000000	.687000000	.716000000	.674000000
275	.444000000	.468000000	.489000000	.494000000	.564000000	.554000000	.520000000	.452000000	.553000000	.504000000	.530000000	.466000000
270	.328000000	.356000000	.360000000	.365000000	.436000000	.416000000	.396000000	.322000000	.425000000	.372000000	.400000000	.332000000
265	.256000000	.279000000	.281000000	.281000000	.356000000	.325000000	.312000000	.232000000	.342000000	.288000000	.312000000	.240000000
260	.223000000	.235000000	.233000000	.228000000	.294000000	.273000000	.262000000	.179000000	.289000000	.235000000	.260000000	.187000000
255	.207000000	.213000000	.187000000	.197000000	.273000000	.245000000	.224000000	.148000000	.250000000	.198000000	.223000000	.155000000
250	.213000000	.219000000	.198000000	.179000000	.237000000	.233000000	.200000000	.136000000	.222000000	.178000000	.200000000	.141000000
245	.248000000	.242000000	.217000000	.187000000	.228000000	.207000000	.198000000	.144000000	.214000000	.182000000	.197000000	.152000000

TABLE X

REDUCED 4:1 $H_2Ch:Hf$ MATRIX

```
1.570000000 1.332000000 1.498000000 1.493000000 1.520000000 1.525000000 1.476000000 1.513000000 1.495000000 1.422000000 1.506000000 1.527000000
 .000000000  .208491719  .009081528  .008364968  .009834394  .006550955  .108328662  .009231210  .007251592  .172389809  .026628025  .005437579
 .000000000  .000000000  .124724695  .001669057  .090172485  .077233096  .028152566  .108394095  .057643053  .018312404  .044093324  .077207092
 .000000000  .000000000  .000000000  .050110681 -.006073636 -.004522942 -.004688536 -.010589240  .025850178 -.000953462  .023930664  .001745935
 .000000000  .000000000  .000000000  .000000000 -.028979344 -.009942892 -.017911789  .003349484 -.021767186  .012464619  .002128382  .002397669
 .000000000  .000000000  .000000000  .000000000  .000000000  .036437758  .003926456 -.005597624  .013756373 -.029369088  .008895092 -.007775979
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.026946952 -.009992103 -.006390569 -.011156278 -.000855973 -.005913944
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .025869500 -.010588855  .003198693 -.000727766  .011395105
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .023542729  .007441420  .006257927 -.010041200
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.020847678 -.014586373  .005912784
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .008905036 -.002160854
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.003645865
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.001309693
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.004354166
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.000823942
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .002065011
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.000754506
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .006914923
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.000870100
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000247175
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .001282712
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REDUCED S MATRIX

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 .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000
 .000000000  .032837879  .034609630  .034554628  .034852775  .034908291  .034368347  .034775211  .034576617  .033784251  .034697833  .034930524
 .000000000  .000000000  .036051598  .035989735  .036309713  .036347555  .039935062  .036224801  .036006117  .045110056  .036375492  .036365753
 .000000000  .000000000  .000000000  .049113651  .060989402  .058205259  .055612575  .065353705  .054136995  .061976541  .052594184  .058221054
 .000000000  .000000000  .000000000  .000000000  .089489057  .085246161  .081490553  .096635188  .087288323  .090517674  .084097131  .085059781
 .000000000  .000000000  .000000000  .000000000  .000000000  .112563238  .122355519  .120737841  .136866962  .122196943  .104794384  .106071301
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .073726413  .073135532  .085933027  .091259364  .064961098  .065213034
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 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .111920709
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .133438359
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .120584620
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .113018435
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .174152326
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .127801353
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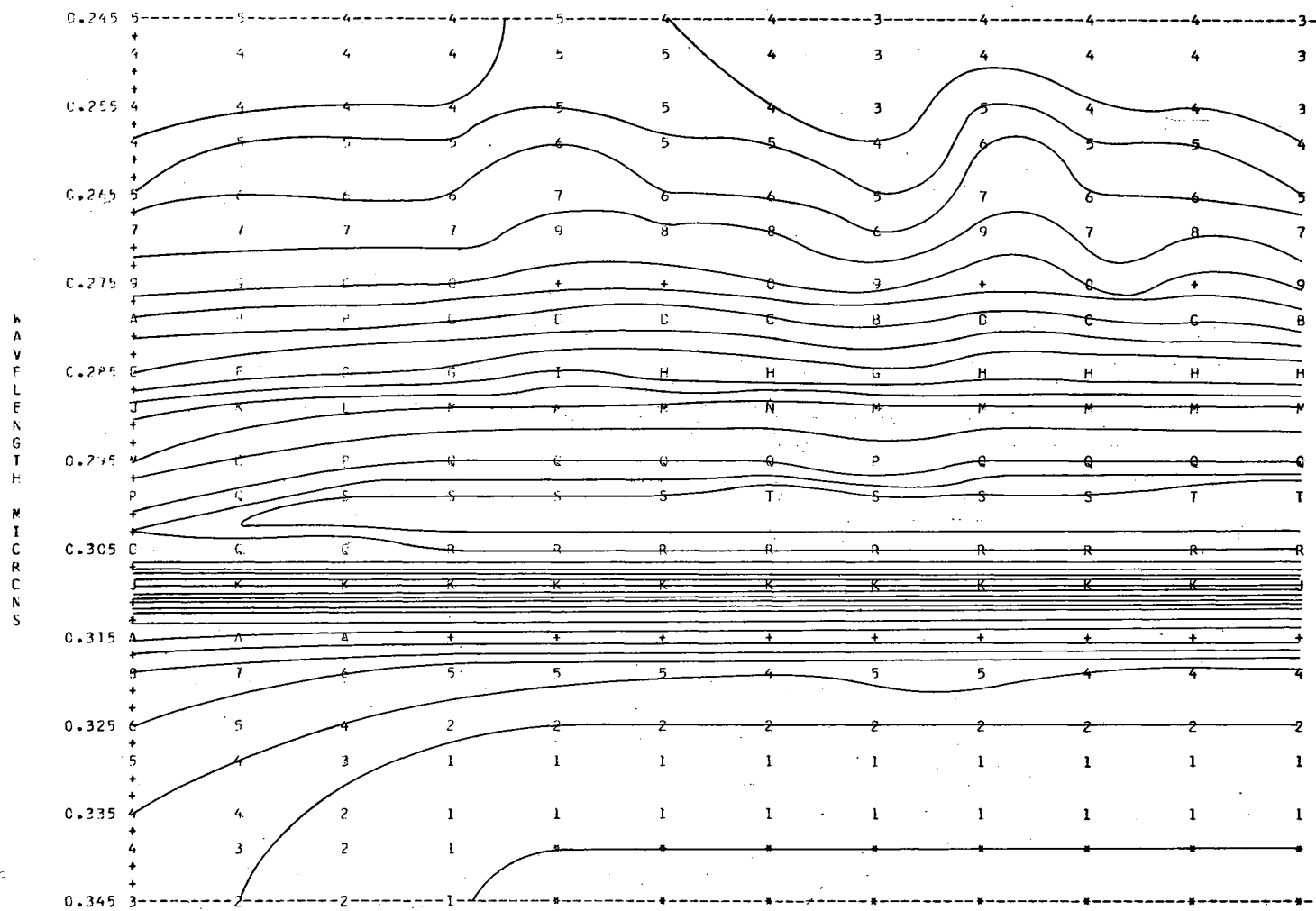
Figure 6. Contour Map of the 4:1 $H_2Ch:Hf$ Plus F^- Absorbances of Table IX

TABLE XI

0.80×10^{-4} M H_2Ch PLUS F^- ABSORBANCE MATRIX FOR SOLUTIONS OF TABLE II

345	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000
340	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000
335	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
330	.042000000	.042000000	.042000000	.042000000	.042000000	.042000000	.042000000	.042000000	.042000000	.042000000	.042000000	.042000000
325	.088000000	.088000000	.088000000	.088000000	.088000000	.088000000	.088000000	.088000000	.088000000	.088000000	.088000000	.088000000
320	.216000000	.216000000	.216000000	.216000000	.216000000	.216000000	.216000000	.216000000	.216000000	.216000000	.216000000	.216000000
315	.545000000	.545000000	.545000000	.545000000	.545000000	.545000000	.545000000	.545000000	.545000000	.545000000	.545000000	.545000000
310	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000	1.064000000
305	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000	1.451000000
300	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000	1.494000000
295	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000	1.388000000
290	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000	1.178000000
285	.905000000	.905000000	.905000000	.905000000	.905000000	.905000000	.905000000	.905000000	.905000000	.905000000	.905000000	.905000000
280	.636000000	.636000000	.636000000	.636000000	.636000000	.636000000	.636000000	.636000000	.636000000	.636000000	.636000000	.636000000
275	.438000000	.438000000	.438000000	.438000000	.438000000	.438000000	.438000000	.438000000	.438000000	.438000000	.438000000	.438000000
270	.300000000	.300000000	.300000000	.300000000	.300000000	.300000000	.300000000	.300000000	.300000000	.300000000	.300000000	.300000000
265	.208000000	.208000000	.208000000	.208000000	.208000000	.208000000	.208000000	.208000000	.208000000	.208000000	.208000000	.208000000
260	.160000000	.160000000	.160000000	.160000000	.160000000	.160000000	.160000000	.160000000	.160000000	.160000000	.160000000	.160000000
255	.128000000	.128000000	.128000000	.128000000	.128000000	.128000000	.128000000	.128000000	.128000000	.128000000	.128000000	.128000000
250	.118000000	.118000000	.118000000	.118000000	.118000000	.118000000	.118000000	.118000000	.118000000	.118000000	.118000000	.118000000
245	.127000000	.127000000	.127000000	.127000000	.127000000	.127000000	.127000000	.127000000	.127000000	.127000000	.127000000	.127000000

TABLE XII

REDUCED 0.80×10^{-4} M H_2Ch PLUS F^- MATRIX

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1.494000000 1.494000000 1.494000000 1.494000000 1.494000000 1.494000000 1.494000000 1.494000000 1.494000000 1.494000000 1.494000000 1.494000000
.000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000
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.000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000 .000000000
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REDUCED S MATRIX

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.025000000 .025000000 .025000000 .025000000 .025000000 .025000000 .025000000 .025000000 .025000000 .025000000 .025000000 .025000000 .025000000
.000000000 .035357905 .035357905 .035357905 .035357905 .035357905 .035357905 .035357905 .035357905 .035357905 .035357905 .035357905 .035357905
.000000000 .035360288 .035360288 .035360288 .035360288 .035360288 .035360288 .035360288 .035360288 .035360288 .035360288 .035360288 .035360288
.000000000 .035369307 .035369307 .035369307 .035369307 .035369307 .035369307 .035369307 .035369307 .035369307 .035369307 .035369307 .035369307
.000000000 .035416618 .035416618 .035416618 .035416618 .035416618 .035416618 .035416618 .035416618 .035416618 .035416618 .035416618 .035416618
.000000000 .035722942 .035722942 .035722942 .035722942 .035722942 .035722942 .035722942 .035722942 .035722942 .035722942 .035722942 .035722942
.000000000 .037634318 .037634318 .037634318 .037634318 .037634318 .037634318 .037634318 .037634318 .037634318 .037634318 .037634318 .037634318
.000000000 .043405116 .043405116 .043405116 .043405116 .043405116 .043405116 .043405116 .043405116 .043405116 .043405116 .043405116 .043405116
.000000000 .049285707 .049285707 .049285707 .049285707 .049285707 .049285707 .049285707 .049285707 .049285707 .049285707 .049285707 .049285707
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.000000000 .045023774 .045023774 .045023774 .045023774 .045023774 .045023774 .045023774 .045023774 .045023774 .045023774 .045023774 .045023774
.000000000 .041336133 .041336133 .041336133 .041336133 .041336133 .041336133 .041336133 .041336133 .041336133 .041336133 .041336133 .041336133
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.000000000 .035465445 .035465445 .035465445 .035465445 .035465445 .035465445 .035465445 .035465445 .035465445 .035465445 .035465445 .035465445
.000000000 .035482850 .035482850 .035482850 .035482850 .035482850 .035482850 .035482850 .035482850 .035482850 .035482850 .035482850 .035482850
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Figure 7. Contour Map of 0.80×10^{-4}M H_2Ch Plus F^- Absorbances of Table XI

TABLE XIII

7.33:1 H_2Ch:Hf PLUS F^- ABSORPTION MATRIX FOR SOLUTIONS OF TABLE III

345	.088000000	.082000000	.056000000	.024000000	.021000000	.018000000	.018000000	.018000000	.019000000	.022000000	.021000000	.017000000
340	.112000000	.105000000	.071000000	.032000000	.023000000	.023000000	.022000000	.022000000	.023000000	.023000000	.022000000	.019000000
335	.138000000	.128000000	.088000000	.042000000	.031000000	.031000000	.031000000	.031000000	.031000000	.032000000	.028000000	.028000000
330	.167000000	.156000000	.111000000	.062000000	.052000000	.052000000	.053000000	.050000000	.052000000	.053000000	.051000000	.048000000
325	.216000000	.206000000	.161000000	.113000000	.102000000	.102000000	.102000000	.099000000	.103000000	.100000000	.098000000	.098000000
320	.344000000	.334000000	.298000000	.257000000	.248000000	.245000000	.247000000	.246000000	.248000000	.242000000	.240000000	.242000000
315	.657000000	.650000000	.623000000	.610000000	.603000000	.609000000	.607000000	.600000000	.605000000	.595000000	.590000000	.577000000
310	1.187000000	1.165000000	1.138000000	1.192000000	1.170000000	1.170000000	1.151000000	1.166000000	1.159000000	1.137000000	1.126000000	1.108000000
305	1.605000000	1.522000000	1.472000000	1.578000000	1.577000000	1.537000000	1.526000000	1.544000000	1.522000000	1.515000000	1.438000000	1.456000000
300	1.568000000	1.568000000	1.534000000	1.642000000	1.621000000	1.603000000	1.590000000	1.600000000	1.595000000	1.524000000	1.494000000	1.530000000
295	1.436000000	1.434000000	1.413000000	1.515000000	1.475000000	1.488000000	1.466000000	1.494000000	1.490000000	1.470000000	1.435000000	1.456000000
290	1.217000000	1.235000000	1.231000000	1.303000000	1.277000000	1.287000000	1.270000000	1.290000000	1.286000000	1.279000000	1.274000000	1.275000000
285	.960000000	.945000000	.940000000	.980000000	.990000000	.990000000	.966000000	.985000000	.985000000	.983000000	.975000000	.970000000
280	.673000000	.665000000	.659000000	.677000000	.690000000	.680000000	.676000000	.688000000	.685000000	.686000000	.685000000	.693000000
275	.463000000	.450000000	.440000000	.452000000	.456000000	.454000000	.454000000	.464000000	.460000000	.458000000	.458000000	.464000000
270	.318000000	.294000000	.292000000	.288000000	.293000000	.290000000	.296000000	.300000000	.302000000	.298000000	.300000000	.295000000
265	.223000000	.198000000	.195000000	.185000000	.188000000	.186000000	.190000000	.198000000	.208000000	.192000000	.192000000	.192000000
260	.173000000	.147000000	.139000000	.129000000	.131000000	.130000000	.133000000	.141000000	.152000000	.136000000	.133000000	.127000000
255	.151000000	.124000000	.112000000	.103000000	.103000000	.102000000	.105000000	.110000000	.122000000	.107000000	.102000000	.102000000
250	.153000000	.130000000	.114000000	.093000000	.097000000	.094000000	.098000000	.100000000	.112000000	.100000000	.095000000	.093000000
245	.188000000	.166000000	.140000000	.100000000	.116000000	.114000000	.117000000	.122000000	.130000000	.123000000	.115000000	.114000000

TABLE XIV

REDUCED 7.33:1 H$_2$Ch:Hf MATRIX

```
1.642000000 1.568000000 1.494000000 1.568000000 1.595000000 1.530000000 1.621000000 1.524000000 1.603000000 1.600000000 1.590000000 1.534000000
 .000000000  .108092570 -.004814859  .098092570 -.006765529 -.007292326 -.009554811 -.004879415 -.008316077 -.011109622 -.007421437 -.055432399
 .000000000  .000000000  .087229525  .015476449  .018589274  .059036724 -.011746771  .068406901  .012849629  .017525298  .006391474  .027691449
 .000000000  .000000000  .000000000 -.075094311 -.006097745 -.012214292  .028743439  .049652473  .003055902  .015120800  .004225916 -.054621333
 .000000000  .000000000  .000000000  .000000000  .034153622  .011019030  .022189010  .000110783  .018597627  .024701452  .023419436  .003614431
 .000000000  .000000000  .000000000  .000000000  .000000000 -.023826304 -.004234559 -.018011182  .004284292 -.002120129 -.002411766  .004250265
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.024379164  .006620877 -.003325680 -.002632595 -.011818470  .004966924
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.019004410 -.008864404 -.006283430 -.001145496  .008799094
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .012428885 -.002928016 -.007969745 -.002207250
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .010428834  .010168857 -.006471119
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .014817130  .004234515
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .003940657
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.000378672
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .001121778
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000297155
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000752519
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .005640977
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.003701030
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.006007969
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000 -.004876084
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .001593757
```

REDUCED S MATRIX

```
 .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000  .025000000
 .000000000  .034649601  .033879500  .034649601  .034935447  .034251655  .035213071  .034189297  .035020625  .034988658  .034882322  .034293300
 .000000000  .000000000  .044033087  .060750084  .045445769  .044574099  .045891526  .044436119  .045600584  .045662243  .045394684  .050146798
 .000000000  .000000000  .000000000  .078204371  .059249136  .068460437  .059081340  .071853174  .058808832  .059385604  .058106072  .066468373
 .000000000  .000000000  .000000000  .000000000  .051746109  .060467933  .057515046  .076874375  .051143798  .053352159  .050603325  .075971961
 .000000000  .000000000  .000000000  .000000000  .000000000  .068503154  .072750495  .083949053  .063765790  .071167072  .067491500  .083178645
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .079184195  .105886243  .069718481  .076678047  .072833954  .090251293
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 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .117979347  .115693671  .112380556  .142119012
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 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .106805729  .000000000  .191965711  .184269794
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .123065829
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .107568910
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .279544979
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .112551373
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .230506194
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .113585344
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .205793549
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .206545085
 .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .000000000  .194851535
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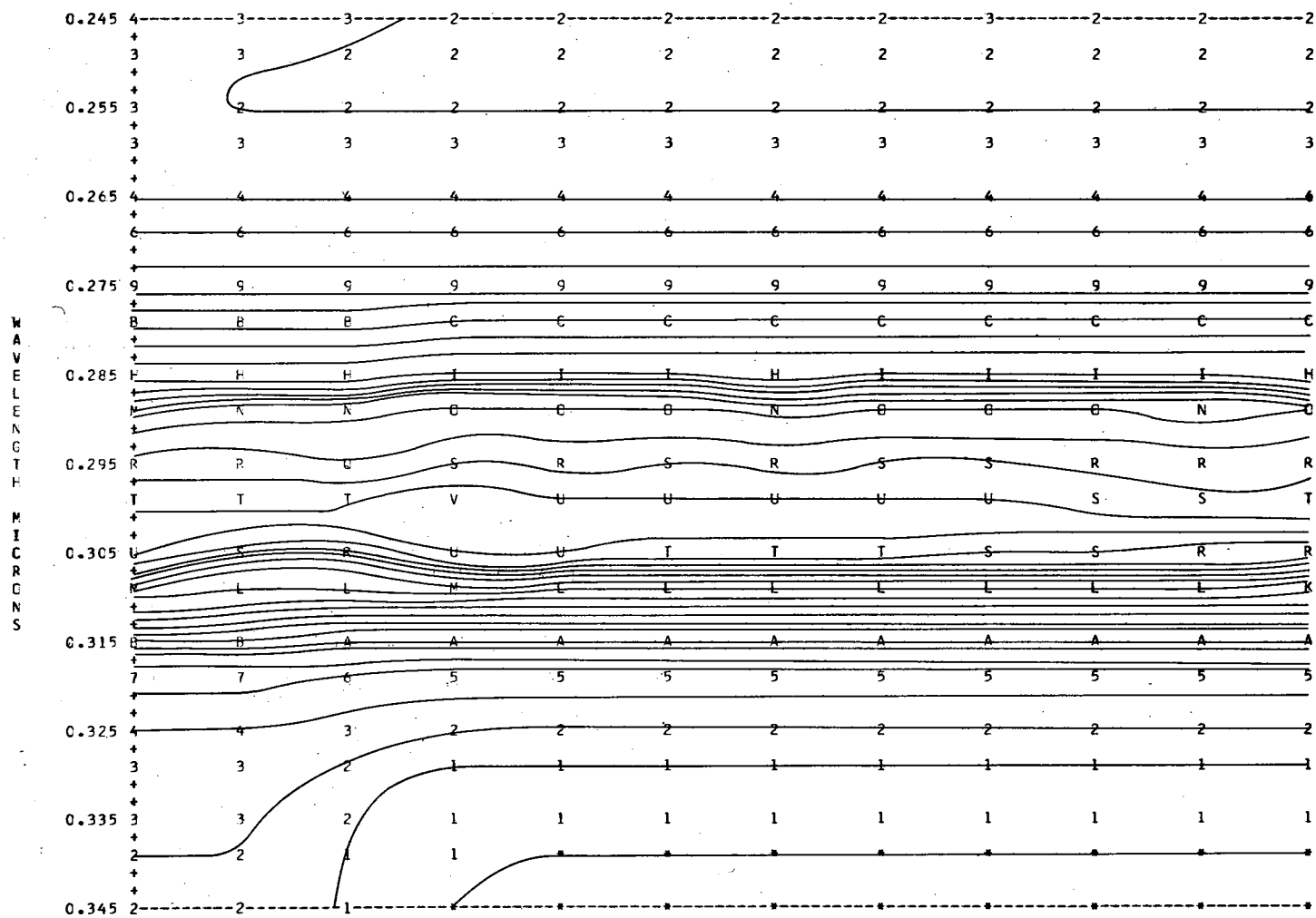
Figure 8. Contour Map of the 7.33:1 $H_2Ch:Hf$ Plus F^- Absorbances of Table XIII

TABLE XV

0.88×10^{-4}M H_2Ch PLUS F$^-$ ABSORBANCE MATRIX FOR SOLUTIONS OF TABLE III

345	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000	.018000000
340	.022000000	.022000000	.022000000	.022000000	.022000000	.022000000	.022000000	.022000000	.022000000	.022000000	.022000000	.022000000
335	.031000000	.031000000	.031000000	.031000000	.031000000	.031000000	.031000000	.031000000	.031000000	.031000000	.031000000	.031000000
330	.052000000	.052000000	.052000000	.052000000	.052000000	.052000000	.052000000	.052000000	.052000000	.052000000	.052000000	.052000000
325	.100000000	.100000000	.100000000	.100000000	.100000000	.100000000	.100000000	.100000000	.100000000	.100000000	.100000000	.100000000
320	.235000000	.235000000	.235000000	.235000000	.235000000	.235000000	.235000000	.235000000	.235000000	.235000000	.235000000	.235000000
315	.575000000	.575000000	.575000000	.575000000	.575000000	.575000000	.575000000	.575000000	.575000000	.575000000	.575000000	.575000000
310	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000	1.094000000
305	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000	1.418000000
300	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000
295	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000	1.427000000
290	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000	1.260000000
285	.970000000	.970000000	.970000000	.970000000	.970000000	.970000000	.970000000	.970000000	.970000000	.970000000	.970000000	.970000000
280	.678000000	.678000000	.678000000	.678000000	.678000000	.678000000	.678000000	.678000000	.678000000	.678000000	.678000000	.678000000
275	.460000000	.460000000	.460000000	.460000000	.460000000	.460000000	.460000000	.460000000	.460000000	.460000000	.460000000	.460000000
270	.297000000	.297000000	.297000000	.297000000	.297000000	.297000000	.297000000	.297000000	.297000000	.297000000	.297000000	.297000000
265	.194000000	.194000000	.194000000	.194000000	.194000000	.194000000	.194000000	.194000000	.194000000	.194000000	.194000000	.194000000
260	.137000000	.137000000	.137000000	.137000000	.137000000	.137000000	.137000000	.137000000	.137000000	.137000000	.137000000	.137000000
255	.107000000	.107000000	.107000000	.107000000	.107000000	.107000000	.107000000	.107000000	.107000000	.107000000	.107000000	.107000000
250	.097000000	.097000000	.097000000	.097000000	.097000000	.097000000	.097000000	.097000000	.097000000	.097000000	.097000000	.097000000
245	.115000000	.115000000	.115000000	.115000000	.115000000	.115000000	.115000000	.115000000	.115000000	.115000000	.115000000	.115000000

TABLE XVI

REDUCED 0.88×10^{-4} M H_2Ch PLUS F^- MATRIX

1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000	1.484000000

|												
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
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.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000
.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000	.000000000

REDUCED S MATRIX

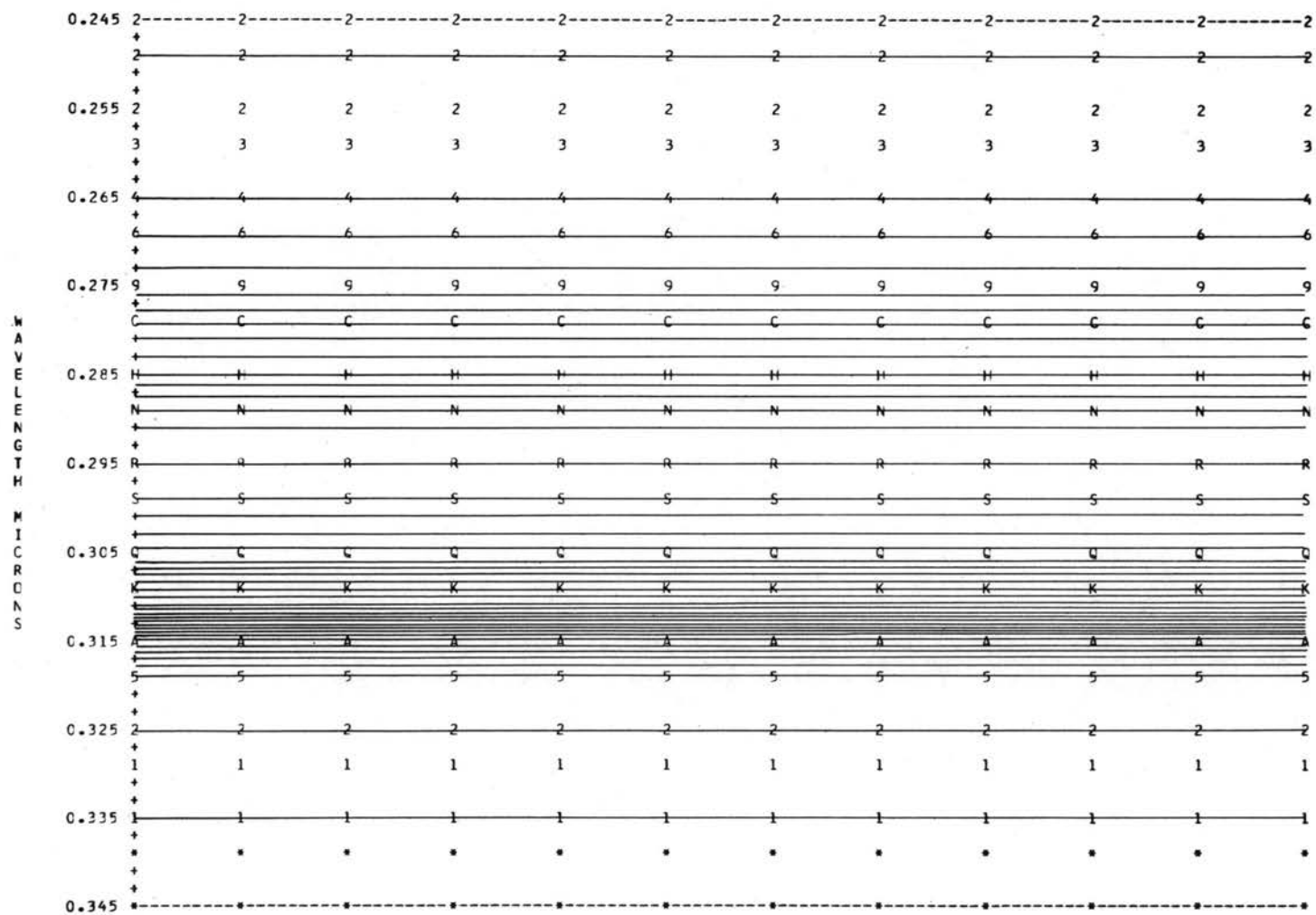|												
.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000	.025000000
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.000000000	.035363052	.035363052	.035363052	.035363052	.035363052	.035363052	.035363052	.035363052	.035363052	.035363052	.035363052	.035363052
.000000000	.035377037	.035377037	.035377037	.035377037	.035377037	.035377037	.035377037	.035377037	.035377037	.035377037	.035377037	.035377037
.000000000	.035435518	.035435518	.035435518	.035435518	.035435518	.035435518	.035435518	.035435518	.035435518	.035435518	.035435518	.035435518
.000000000	.035795889	.035795889	.035795889	.035795889	.035795889	.035795889	.035795889	.035795889	.035795889	.035795889	.035795889	.035795889
.000000000	.037916522	.037916522	.037916522	.037916522	.037916522	.037916522	.037916522	.037916522	.037916522	.037916522	.037916522	.037916522
.000000000	.043924069	.043924069	.043924069	.043924069	.043924069	.043924069	.043924069	.043924069	.043924069	.043924069	.043924069	.043924069
.000000000	.048900782	.048900781	.048900782	.048900782	.048900782	.048900781	.048900782	.048900782	.048900782	.048900782	.048900782	.048900781
.000000000	.035357939	.035357939	.035357939	.035357939	.035357939	.035357939	.035357939	.035357939	.035357939	.035357939	.035357939	.035357939
.000000000	.049049157	.049049157	.049049157	.049049157	.049049157	.049049157	.049049157	.049049157	.049049157	.049049157	.049049157	.049049157
.000000000	.046380183	.046380183	.046380183	.046380183	.046380183	.046380183	.046380183	.046380183	.046380183	.046380183	.046380183	.046380183
.000000000	.042238070	.042238070	.042238070	.042238070	.042238070	.042238070	.042238070	.042238070	.042238070	.042238070	.042238070	.042238070
.000000000	.038870509	.038870509	.038870509	.038870509	.038870509	.038870509	.038870509	.038870509	.038870509	.038870509	.038870509	.038870509
.000000000	.037014917	.037014917	.037014917	.037014917	.037014917	.037014917	.037014917	.037014917	.037014917	.037014917	.037014917	.037014917
.000000000	.036056447	.036056447	.036056447	.036056447	.036056447	.036056447	.036056447	.036056447	.036056447	.036056447	.036056447	.036056447
.000000000	.035656166	.035656166	.035656166	.035656166	.035656166	.035656166	.035656166	.035656166	.035656166	.035656166	.035656166	.035656166
.000000000	.035505679	.035505679	.035505679	.035505679	.035505679	.035505679	.035505679	.035505679	.035505679	.035505679	.035505679	.035505679
.000000000	.035447121	.035447121	.035447121	.035447121	.035447121	.035447121	.035447121	.035447121	.035447121	.035447121	.035447121	.035447121
.000000000	.035430785	.035430785	.035430785	.035430785	.035430785	.035430785	.035430785	.035430785	.035430785	.035430785	.035430785	.035430785
.000000000	.035461338	.035461338	.035461338	.035461338	.035461338	.035461338	.035461338	.035461338	.035461338	.035461338	.035461338	.035461338

Figure 9. Contour Map of the 0.88×10^{-4}M H_2Ch Plus F^- Absorbances of Table XV
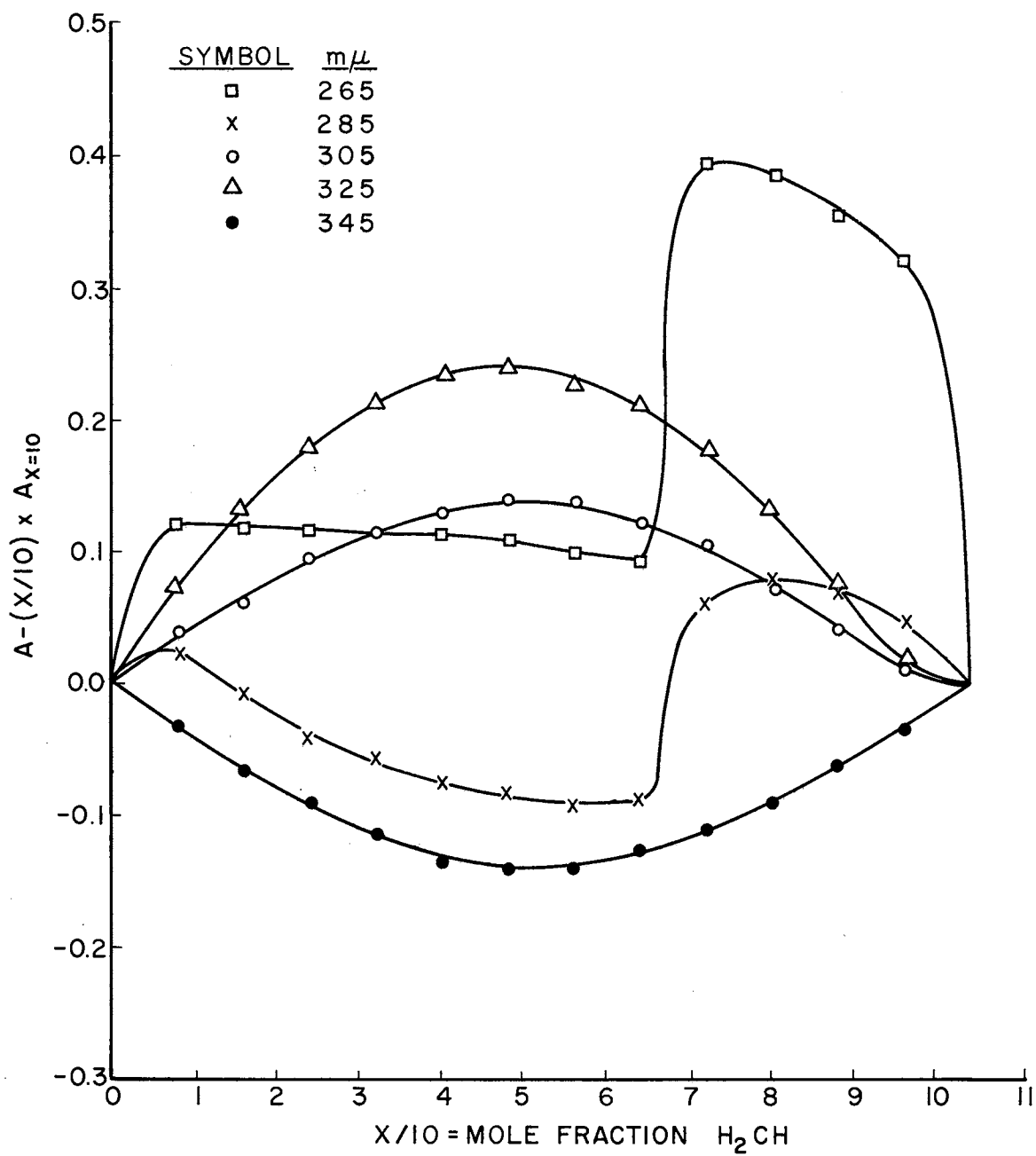
Figure 10. Job Plots of H_2Ch-Hf Systems at Selected Wavelengths

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Appendix A

Rank Program for 1410

```
      MON$$       JOB   221150006
      MON$$       ASGN  MGO,A2
      MON$$       ASGN  MJB,A3
      MON$$       MODE  GO,TEST
      MON$$       EXEQ  FORTRAN,,,10,10,,,VEATCH
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 DECI7AL POINT)
C          EXPERIMENT 2 DATA FOLLOWS IMMEDIATELY AND SO ON
C
C
      DIMENSIONA(25,18),S(25,18)
C
    1 FORMAT(2I5,F9.8)
00002 FORMAT(16(F4.3,1X))
    3 FORMAT (1H2,10X,17HRANK OF SYSTEM IS,I3,1X,31H /ITHIN A
     1RANGE OF PLUS OR MINUS,F15.5,1X,12HSIGMA LIMIT;)
    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)
   50 READ(1,1)N,L,CRIT
      DO10J=1,N
00010 READ(1,2)(A(I,J),I=1,L)
      ERROR=0.025
      DO 14 I=1,L
      DO 14 J=1,N
   14 S(I,J) = ERROR
      WRITE(3,4)
      DO20I=1,L
```

```
   20 WRITE(3,8)(A(I,J),J=1,N)
      WRITE(3,5)
      DO30I=1,L
   30 WRITE(3,8)(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+
     12+(S(JC,JC)*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(3,3)NRANK,CRIT
      WRITE(3,6)
      DO165I=1,L
  165 WRITE(3,8)(A(I,J),J=1,N)
      WRITE(3,7)
      DO170 I=1,L
  170 WRITE(3,8)(S(I,J),J=1,N)
      GO TO 50
      END
      MON$$      EXEQ LINKLOAD
                 PHASEONE
                 CALL VEATCH
      MON$$      EXEQ ONE,MJB
  00012000210001
      DATA OF ABSORBANCE VALUES
```

Appendix B

Plot Program for 7040

```
$JOB                    FRED VEATCH                221150006
$ID          S-001
$IBJOB RANK     NODECK
$IBFTC MAIN     NODECK
      DIMENSION X(252),Y(252),Z(252),XX(12),YY(21)
    1 FORMAT(16(F4.3,1X))
    2 CL=0.0
      CM=25.0
      DO50I=1,12
      CL=CL+2.
      CM=CM-2.
   50 XX(I)=CL/(CL+CM)
      YY(1)=.360
      DO20 I=2,21
   20 YY(I)=YY(I-1)-.005
      DO51 I=1,21
      Y(I)=YY(I)
   51 X(I)=XX(1)
      DO52 I=22,42
      Y(I)=YY(I-21)
   52 X(I)=XX(2)
      DO53 I=43,63
      Y(I)=YY(I-42)
   53 X(I)=XX(3)
      DO54 I=64,84
      Y(I)=YY(I-63)
   54 X(I)=XX(4)
      DO55 I=85,105
      Y(I)=YY(I-84)
   55 X(I)=XX(5)
      DO56 I=106,126
      Y(I)=YY(I-105)
   56 X(I)=XX(6)
      DO57I=127,147
      Y(I)=YY(I-126)
   57 X(I)=XX(7)
      DO58I=148,168
      Y(I)=YY(I-147)
   58 X(I)=XX(8)
      DO59I=169,189
      Y(I)=YY(I-168)
   59 X(I)=XX(9)
      DO60I=190,210
      Y(I)=YY(I-189)
   60 X(I)=XX(10)
      DO61I=211,231
      Y(I)=YY(I-210)
   61 X(I)=XX(11)
      DO62I=232,252
      Y(I)=YY(I-231)
   62 X(I)=XX(12)
      L=1
      DO110I=1,12
      K=L+20
```

63

```
         READ(5,1)(Z(J),J=L,K)
  110 L=L+21
         DO210I=1,252
  210 IF(Z(I).LT.0.0)Z(I)=0.0
         CALL PLOT(X,.080,1.04,0,Y,.360,.260,0,Z,0.0,2.0,0,252,1,2,3,3)
         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(13),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(9X,F6.3,11(4X,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(13)=XMAX
         U=XMIN
         DO16K=2,12
         U=(XMAX-XMIN)/12.+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=13,133,10
   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=1,12)
      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
$ENTRY
      ABSORBANCE DATA
           ABSORBANCE VERSES WAVELENGTH AND SOLUTION CONC   HF-CH SYSTEM
WAVELENGTH MICRONS*1234567890+ABCDEFGHIJKLMNOPQRSTUVWXYZ/$TOTAL CH *(E+04)
$IBSYS
```

Appendix C

Flow Diagram of Iterative Program

READ

$Ab(21,12)$, $MA_3(12)$, $Ab_4(21)$

$C_A(12)$, $C_M(12)$, $\epsilon_A(21)$

$$(A)(12) = \frac{Ab(12) \text{ at } 300 \text{ m}\mu}{\epsilon_A \text{ at } 300 \text{ m}\mu}$$

$$\bar{n}(12) = \frac{C_A(12) - (A)(12)}{C_M(12)}$$

$$(MA) = \bar{n}_4 \times C_{M_4}$$

$$\epsilon_1(21) = \frac{Ab_4(21) - \epsilon_L(21) \times (A)_4}{(MA)}$$

$$\epsilon_M(21,12) = \frac{Ab(21,12) - \epsilon_A(21) \times A(12)}{C_M(12)}$$

A   B

$$(MA) = C_A(12) - A(12) - 3(MA_3)$$

$$(MA_3) = \frac{\bar{n}(12) \times C_M(12) - (MA)}{3}$$

$$(M) = C_M(12) - (MA) - (MA_3)$$

$$\beta_1(12) = \frac{(MA)}{(M) \times A(12)}$$

$$\beta_3(12) = \frac{(MA_3)}{(M) \times [A(12)]^3}$$

$$\epsilon_3(12) = \frac{\epsilon_M(21,12)\left[1+\beta_1(12) \times A(12)+\beta_3(12) \times [A(12)]^3\right]}{\beta_3(12) \times [A(12)]^3}$$

$$- \frac{\epsilon_1(21) \times \beta_1(12) \times A(12)}{\beta_3(12) \times [A(12)]^3}$$

$$\bar{n}(12) = \frac{\beta_1(12) \times A(12) + 3\beta_3(12) \times [A(12)]^3}{1+\beta_1(12) \times A(12) + \beta_3(12) \times [A(12)]^3}$$

$$MA_3 = \frac{\epsilon_M(21,12) \times C_M(12) - \epsilon_1(21) \times (MA)}{\epsilon_3(12)}$$

Have

25 iterations

been made?

No

Yes

A   B

Print (M), (MA), (MA$_3$), β_1(12), β_3(12), π(12), ϵ_3(12)

Have all 12 solutions been run?   No

Yes

Print average values of ϵ_3, β_1 and β_3

Have all 21 wavelengths been run?   No

Yes

Print grand average value of β_1 and β_3

VITA

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Candidate for Degree of

Master of Science

Thesis: COMPUTER INTERPRETATION OF SPECTROPHOTOMETRIC DATA OF HAFNIUM-CHLORANILIC ACID COMPLEXES IN 3M PERCHLORIC ACID MEDIUM

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