STABILITY CONSTANTS OF TIN-PYROCATECHOL VIOLET COMPLEXES FROM COMPUTER ANALYSIS OF SPECTRAL DATA

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PREFACE

This study was made to develop a generally applicable, objective computer method for determining the number, nature, and stabilities of complexes in solution from spectrophotometric data.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Studies of the absorption of visible and ultraviolet radiation have long been used to obtain information about equilibria in solution. However, since the optical absorbance of a solution is governed by a characteristic intensive factor, the extinction coefficient, as well as by the concentration of each absorbing species, interpretation of measurements of this type is complicated if several complexes coexist. Many spectrophotometric methods used in quantitative analysis have been developed without complete knowledge of the nature and properties of the absorbing species. Therefore, unambiguous methods for the determination of the number, nature, and stabilities of several absorbing species in solution are needed.

Adequate experimental and theoretical descriptions of the chemistry of natural water systems are difficult to formulate. In order to develop a chemical model of a natural water system which would be useful for water quality definition and control, detailed information concerning accurate knowledge of the chemical equilibria is necessary. The concentrations of species in solution can be calculated from the measured concentrations of selected ions and the equilibria relating them provided reasonably accurate values of the concentration formation constants are known for the particular environment under study. The computer methods described in this work provide a valuable method for determining the number, composition, and stabilities of species in solution in a straightforward, objective manner with a degree of accuracy and precision required of these numbers for modeling natural water systems. The methods are described using spectrophotometric data but could be applied to concentration data obtained in studies of natural waters by most other methods.

The purpose of this work was to develop a generally applicable, objective, computer method for determining the number, nature, and stabilities of complexes in solution from spectrophotometric data. Six computer programs are used for the analysis of the absorbance data:

1) Matrix Rank Program
2) Species Number Program
3) Corresponding Solutions Plot Program
4) Corresponding Solutions $\bar{n}$, [L] Program
5) Formation Function Program
6) Pit-Mapping

The matrix rank program calculates the number of components that contribute to the absorption spectrum of a multicomponent system. The species number program determines the number of absorbing species and gives information concerning trends in species number with wavelength or solution composition. The corresponding solutions plot program calculates the corresponding solution functions, E, which are used as input data for Program 4. This program also plots the E functions versus total ligand concentration at each total metal concentration. The corresponding solutions $\bar{n}$, [L] program calculates formation function data using the E functions, total metal and total ligand concentrations, and the extinction coefficients of the ligand as input data. The formation function program calculates stability constants from the $\bar{n}$, $[L]$ data obtained in Program 4 (1). The pit-mapping program calculates stability constants for polynuclear, mononuclear, or mixed mononuclear and polynuclear systems. These programs constitute a generally applicable and objective method for analyzing spectrophotometric data obtained from multicomponent systems.

The final part of this work was to use these programs to analyze spectrophotometric data from an unknown system. The pyrocatechol violet (PCV) complexes of the tin(IV) were chosen for this study. Ross and White (2) have published a procedure for the spectrophotometric determination of tin(IV) using PCV as the colorimetric reagent. Information concerning the stabilities of these complexes has not been published.

The nomenclature used in this work is presented in the following definitions. The overall, stoichiometric stability constant, β_{mn}, of the complex, M_mL_n, formed from a central group, M, and ligand, L, is defined by Equation (1).

$$\beta_{mn} = \frac{[M_mL_n]}{[M]^m[L]^n} \tag{1}$$

The total analytical concentrations of the central group, C_M, and the ligand, C_L, are given by Equations (2) and (3), where M and N are the maximum values of m and n in the system.

$$C_M = [M] + \sum_{1}^{M}\sum_{1}^{N} m[M_mL_n] = [M] + \sum_{1}^{M}\sum_{1}^{N} m\beta_{mn}[M]^m[L]^n \tag{2}$$

$$C_L = [L] + \sum_{1}^{M}\sum_{1}^{N} n[M_mL_n] = [L] + \sum_{1}^{M}\sum_{1}^{N} n\beta_{mn}[M]^m[L]^n \tag{3}$$

The degree of formation of the system or the average number of ligands bound to the central group, $\bar{n}$, is defined in Equation (4).

$$\bar{n} = \frac{C_L - [L]}{C_M} = \frac{\sum_{1}^{M} \sum_{1}^{N} n\beta_{mn}[M]^m[L]^n}{\sum_{1}^{M} \sum_{0}^{N} m\beta_{mn}[M]^m[L]^n} \qquad (4)$$

The fraction of the ligand, a polyprotic acid, present as each species is the ratio of the concentration of that species to the analytical concentration.

$$\alpha_c = \frac{[H_cL]}{C_L} \qquad (5)$$

The absorbance of a solution which contains the species L, M, and M_mL_n is given by Equation (6), where 1 is the path length and ϵ_{mn} is the molar extinction coefficient of species M_mL_n.

$$A = 1(\epsilon_L[L] + \epsilon_M[M] + \sum_{1}^{M} \sum_{1}^{N} \epsilon_{mn}[M_mL_n]) \qquad (6)$$

CHAPTER II

LITERATURE REVIEW

The choice of a method for determining the number and composition of absorbing species and for computing stability constants from spectrophotometric data is governed by the complexity of the system and by the number of extinction coefficients which can be determined independently. It is difficult to interpret measurements of A and $[L]$ unambiguously except in the simplest cases. More satisfactory results can be obtained in cases where it is possible to calculate the functions $\bar{n}$, $[L]$ or α_c, $[L]$ from spectrophotometric data.

Graphical Methods

A number of methods which are still widely used to determine the formulas and stability constants of complexes were first designed for the case in which only one complex is formed. The physical property most often measured has been optical absorbance although other physical properties which involve intensive factors have been used. The method of continuous variations was first applied to the formation of complexes in solution by Job (3) who assumed that only one complex was present. The experimental parameter used in this method is the difference, Y, between some measured physical property of an equilibrium mixture of ligand and central ion in solution and the value the property would have if no reaction occurred. A plot of Y versus solution composition should have a maximum or minimum at the mole fraction corresponding to the composition of the complex formed if only one complex is present (4). If a system contains more than a single complex, the concentration of any given complex will reach a maximum at some value of the molar ratio of the reactants that differs from that found in the complex (5). This method has been used to obtain information concerning the formulas of complexes present in multi-component systems although Vosburgh and Cooper (4) state that caution is necessary in such cases since the results obtained depend upon the wavelength of light used. Job (3), Hagenmuller (6), Schaeppi and Treadwell (7), and Schwarzenbach (8) have described graphical methods for calculating the overall stability constant β_n once the value of n has been determined. These methods are not suitable for systems in which n is greater than one. Watkins and Jones (5) conclude that in the general case it is impossible to obtain detailed information on a system containing several successive complexes by the use of the method of continuous variations alone.

The mole-ratio method is of value for obtaining information about the composition of complexes in solution although the results must be interpreted with care (9, 10). Yoe and Jones (9) showed that if the complex formed is slightly dissociated, a plot of absorbance versus mole-ratio, C_L/C_M, for a series of solutions in which C_M is kept constant and C_L is varied, rises steeply from the origin as a straight line for mole ratios below that corresponding to the composition of the complex formed, then breaks sharply to a constant absorbance at the mole-ratio of C_L/C_M in the complex. If more than one complex is formed, and the various complexes have different absorption characteristics and different formation constants, measurements at different wavelengths will reveal their presence by breaks in the mole-ratio plots; even at one wavelength significant changes in slope indicate the presence of different complexes (11). The slope-ratio method is similar and is restricted to the formation of a single complex (10). The curvature of the mole-ratio and continuous variations plots have been used to calculate the stability constant of a single complex but the results are only approximate. These methods have the disadvantage that their usefulness depends upon the stability of the complex being studied.

A graphical method for determining the number of absorbing species is described by Coleman and Varga (12). Absorbance data is arranged in matrix form and various functions are plotted assuming one, two, or three absorbing species. The method is based on the rank of the absorbance matrix. The theory of this method will be described in detail in a later section dealing with computer programs.

A new method for determining the composition of complexes of the form ML_n was described in 1960 by Asmus (13). Later articles modified the method so that it could be used to determine the composition of complexes of the form M_mL_n (14, 15). For the complex M_mL_n, data for the determination of m/n is obtained by varying the excess of the reactant M, the concentration of L being maintained constant. By preparing a second series of solutions in which the concentration of M is kept constant and in excess, while the concentration of L is varied, data for determining n is obtained. Using this absorbance data, curves are plotted for different values of the ratio m/n. A straight line is obtained for the correct value of m/n. The same procedure is then repeated to determine n.

In a review, Bjerrum (16) has pointed out that the formation of complexes in aqueous solution appears to occur in stepwise fashion. The number and nature of complexes formed can sometimes be deduced from the shape of the formation curve. This is a widely used method since many experimental techniques yield data of this type ($\bar{n}$ or α_c as a function of $[L]$). If the formation curve has a limiting value at an integral value N of $\bar{n}$, then it may be assumed that the highest complex present is ML_N. It is often impossible to increase the free ligand concentration to a value such that $\bar{n}$ becomes constant in which case inspection of the formation curve does not immediately indicate the number of complexes.

Irving (17) describes a graphical method for evaluating experimental results that should fit a linear equation. The principle behind this method is to use a coordinate system such that each pair of observations is used to define a straight line. The various straight lines for all the observations are then to intersect in a common point whose coordinates are related to the unknown constants. Irving uses this method to calculate the stability of a single complex, ML, from spectrophotometric data.

The most common graphical method for determining stability constants is the method of linear plots (18). The equations describing the system are transformed so that they are linear in the variables over a certain range of one of the variables. In this range the experimental data can be plotted as straight lines. Under limiting conditions, the intercept of this line on one of the axes, or the slope of the line, gives a value which may be one of the constants or a parameter which is a simple function of the constant. This method has been used to calculate the stability constants for N = 1 and N = 2 where the experimental data is absorbance, A, as a function of [L] (19, 20, 21).

Interpretation is extremely difficult for systems in which three or more complexes are formed. For these systems extrapolation methods described by Newman and Hume (22) are used. They describe a method which uses absorbance data for determining successive formation constants and extinction coefficients for systems containing either single or mixed ligand complexes. The approach is to assume that only the first complex exists in solutions of low free ligand concentration and determining values of ϵ_0, ϵ_1, and β_1 from measurements in this region. These values can then be combined with data for solutions which contain slightly higher ligand concentrations to give values of ϵ_2, β_2 and the process repeated for higher complexes. Alternatively, values of ϵ_N, ϵ_{N-1}, and β_N can be obtained using solutions of high free ligand concentration and the above procedure reversed.

A number of authors have given methods for obtaining stability constants by extrapolation of certain functions to zero free ligand concentration. In each case the function $\bar{n}$ or α_c are transformed to give polynomials in $[L]$ or $[L]^{-1}$ and values of the stability constants can be obtained by extrapolating these functions to $[L] = 0$ or $[L]^{-1} = 0$. The coefficients of these polynomials are the required β_n. The graphical extrapolations reduce the polynomials to N linear equations. Reviews of these methods are given by Sullivan and Hindman (23), and Rossotti and Rossotti (24).

The methods of linear plots and extrapolation are the most used methods for computing stability constants from spectrophotometric data of the type A, [L]. Although the values of ϵ_n and β_n may be refined by successive approximation, considerable uncertainty often exists in stability constants computed by extrapolation methods (25). More satisfactory values may be obtained in cases where it is possible to calculate the functions $\bar{n}$ or α_c from spectrophotometric data using the method of corresponding solutions. The theory of this method will be presented in detail in a later section.

The method of linear plots is also widely used for the analysis of the data $\bar{n}$, [L] (24, 25). Another method of treating this data is the method of curve fitting. Values of stability constants can be obtained by comparing experimental formation curves with curves calculated from Equation (4) using different values of β_n. This method is particularly useful for cases in which one or two complexes are formed. If three or more complexes are formed, a large number of formation curves would be necessary to fit the data and only approximate values of the constants would be obtained.

Computer Methods

The use of computers for the determination of the number and nature of complexes in solution has been quite limited. Matrix rank calculations for the analysis of absorption spectra of multicomponent systems and contour mapping of the absorbance data (three dimensional plotting) are the only methods in common usage.

The original paper dealing with matrix rank analysis was by Wallace (26) who applied the method to a system containing organic indicators. Several other papers (27, 28, 29, 30) have been published using the basic ideas presented by Wallace (26). When large amounts of data are obtained, computer calculation of the rank of the absorbance matrix is necessary. A modification of the original matrix rank program is used in the present work (27). The theory of the method and the program changes are given in a later section.

Three dimensional contour plots of absorbance data can be used to provide a visual check on the rank of the absorbance matrix and to give information concerning the composition of the complexes in solution (31). A plotting program allows points having the relationship $Z = g(X,Y)$ to be plotted as a topographic mapping of a three dimensional surface onto the X-Y plane. The wavelength is plotted as the ordinate, concentration as the abscissa, and absorbance as the contours. By inspection the number of peaks and valleys in this plot are obtained and the molar ratios of the reactants where they occur give information concerning the nature of the complexes. This program was used by Varga and Veatch (31) in the interpretation of the hafnium-chloranilic acid system.

The most commonly used method for numerical calculation of stability constants in which the number of measured points exceed the number of unknown constants is the method of least squares (18, 32, 33, 34, 35, 36, 37, 38, 39). The principle of least squares, which is founded on the normal probability equation, says that the best or most probable value of a measured quantity is that for which the sum of the weighted squares of the residuals is a minimum. The application of this principle to curve fitting is extensively treated by Deming (40). The method of least squares does not introduce any systematic computational errors. It gives the best set of constants obtainable from the data according to the theory of error and it also permits the calculation of standard errors of these constants. The determination of many parameters from a large amount of experimental data using the method of least squares leads to very extensive calculations. Therefore, little use of this method had been made until recently when high-speed digital computers became available.

The least squares condition leads to normal equations which can be solved by straightforward methods if the system can be described by a function linear in the unknown stability constants. In studies of stepwise complex formation, if the concentration of the central ion or one of the complexes has been measured, linear equations usually result. Much of the potentiometric, polarographic, ion exchange, and solvent extraction work done on metal complexes has been interpreted using such a model which can be solved by a rigorous non-iterative linear least squares calculation.

The application of least squares methods to spectrophotometric data usually leads to nonlinear equations in the unknowns. If [L], [M], ϵ_L, and ϵ_M can be determined, a least squares calculation gives constants from which β's and extinction coefficients can be determined (41, 42, 43). However, if only [L], ϵ_L, and C_M are known, the equations are nonlinear and difficult to solve.

If the function relating β's and ϵ's is nonlinear in these constants, two general approaches for solution are used. Rydberg (18) outlines the Gauss-Newton iterative method of solution. In order to obtain an equation linear in the unknowns (β's), the β's are replaced by estimated values and their deviations from the true values. The function is then expanded in a Taylor series, neglecting higher terms, and solved for the deviations by the method of least squares. These values of the deviations are used to obtain better values of the β's and this procedure repeated until the deviations of the β's are negligible in comparison to the standard errors of the stability constants. Rabideau and Kline (39) apply this method to the spectrophotometric investigation of the hydrolysis of Pu(IV).

A more systematic method of solving the system is the method of 'pitmapping' described in several papers by Sillen and coworkers (36, 37, 38). In this method approximate stability constants are obtained by graphical methods. Sillen then considers the function $f(\beta_1, \beta_2, \ldots, \beta_n)$. The approximate values are used to study how the sum of squares (SS) of the residuals vary with the variation of one parameter at a time. When the minimum of SS is found for one parameter, this value is retained, and the next parameter is varied until a minimum of SS is found for that parameter. After SS has been minimized for each parameter in turn, the procedure is started over again, and continued in this manner until the sum of squares of the residuals is a minimum for all parameters. However, there is no guarantee that a true minimum will be reached. Sillen (36) states that this method of programming will be applied to spectrophotometric data, which commonly give nonlinear equations and several articles have just been published (44, 45).

If the spectrophotometric method of investigation is the method of corresponding solutions, $\bar{n}$, $[L]$ data is obtained. Several papers discuss the calculation of successive stability constants using formation function data (1, 46, 47, 48, 49, 50). A review of these methods is given by Irving and Rossotti (51). Successive approximations, solution of simultaneous equations, interpolation at half $\bar{n}$ values, Schwarzenbach's Graphical Method, correction-term method, and least squares are some of the techniques reviewed in this paper. Most of the recent work has been done using least squares.

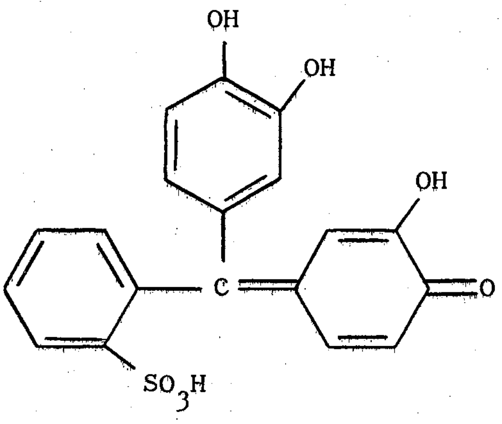
Graphical methods for determining the number and nature of species in solution are generally applicable only to simple systems. However, the mole-ratio method, Coleman and Varga's species number method, and the straight-line method of Holme and Langmyhr give valuable information if the number of absorbing species is three or less. Graphical methods for determining stabilities are even further restricted because of the necessity for determining extinction coefficients as well as stability constants. Usually only approximate constants can be obtained.

The computer methods most widely used are matrix rank and least squares calculations. Matrix rank analysis is an excellent way to determine the number of species in a solution from spectrophotometric data. Linear least squares and iterative calculations are successful in simple systems. For spectrophotometric analysis of multicomponent systems the method of corresponding solutions is superior to other techniques. This method gives formation function data which can be analyzed using linear least squares if the complexes are mononuclear. If polynuclear complexes are formed, nonlinear least squares and iterative techniques must be used.

Tin-Pyrocatechol Violet

Many new reagents for colorimetry have been introduced in the past few years but very few have been applied to the determination of tin. Sandell (52) describes reagents available now as generally unsatisfactory in sensitivity and specificity. Dithiol (52) is considered the most useful, although there are several articles describing methods using phenylfluorone (53, 54, 55). The procedure published recently by Ross and White (2) using pyrocatechol violet (pyrocatechol sulfonphthalein or 3,3',4'-trihydroxyfuchsone-2''-sulfonic acid) is as sensitive and less subject to error than the above procedures. Their results indicate that pyrocatechol violet (PCV) forms complexes with Sn(IV) and not Sn(II). No information is given regarding the stabilities of these complexes.

PCV was first obtained in a pure state in 1954 by Vodak and Leminger (56) who prepared it by the condensation of o-sulfobenzoic anhydride with pyrocatechol. It is a reddish-brown crystalline powder which is readily soluble in water and aqueous ethanol, but insoluble in nonpolar solvents like ether, benzene, and xylene. An aqueous solution of PCV is yellow with the indicator present as a singly charged anion owing to the ionization of the sulfonic acid group.



PCV

PCV shows acid-base indicator properties with color transitions in both acidic and alkaline media. Several equilibria involving dissociation of hydroxyl protons have been described by Suk and Malat (57). Ter- and quadrivalent cations form complexes with PCV in acidic and alkaline media whereas divalent cations, as a rule, form complexes only in alkaline media. Numerous procedures involving the use of PCV as an indicator in chelatometric titrations (57) as well as its use as a spectrophotometric reagent for zirconium (58), iron (59), vanadium (60), yttrium (61), scandium (62), and other metals have been published recently. Very little information concerning the stabilities of the complexes formed is given.

CHAPTER III

MATRIX RANK ANALYSIS

The first step in the computer analysis of absorption spectra is to determine the number of absorbing species in solution. A method was developed by Wallace (26) to find the number of components that contribute to the absorption spectrum of a multicomponent system. The only assumption involved is that Beer's law is valid for each component. The absorption spectra of a series of solutions in which exist a number of absorbing species whose relative concentrations change from one solution to the next are measured. The changes in concentration can be accomplished, for example, by changing the ligand concentration in the formation of inorganic complexes or the pH of solutions containing organic indicators. Beer's law for a multicomponent system is given by Equation (7):

$$A_{\lambda j} = \sum_{k=1}^{m} \epsilon_{\lambda k} C_{kj} \tag{7}$$

where

$A_{\lambda j}$ is the absorbance at wavelength λ in the j^{th} experiment,

$\epsilon_{\lambda k}$ is the extinction coefficient of the k^{th} component at wavelength λ,

C_{kj} is the concentration of component k in the j^{th} experiment, and

m is the total number of components.

Equation (7), from the definition of matrix multiplication, can be written in more compact form where A is a p x n matrix, B is a p x m matrix, and C is a m x n matrix.

$$A = BC \tag{8}$$

p is the number of different wavelengths and n is the number of experiments. The rank, R, of a matrix is defined as the order of the largest nonzero determinant that can be obtained from the elements of the matrix. Since a nonzero determinant requires that the rows and columns be linearly independent, the rank of a matrix is determined by the maximum number of linearly independent rows and columns. Therefore, the rank of a matrix gives the number of linearly independent components.

In general, determinants derived from the B matrix are non-zero, irrespective of order. The rank of the concentration matrix, therefore, determines the rank of the corresponding A matrix. It is a standard theorem that if matrix A is of rank R, then A contains R linearly independent variables with any variables in excess of R being linearly dependent. For a given system, the following relation is valid with C enumerating the number of components in the system and P the number of relationships among them.

$$P + R = C \tag{9}$$

Since in an open system the concentrations of the components are varied arbitrarily, no relationships are present between different components and R = C.

General Outline of Method

The computer method of determining the rank of an absorbance matrix described by Wallace and Katz (27) is an objective analysis based on standard statistical criteria. The method consists of setting up, in addition to the absorbance matrix A, another matrix S whose elements, S_{ij}, are the estimated errors of A_{ij}. A is then reduced by a series of row and column operations to an equivalent reduced matrix, whose elements below the principal diagonal are all zero. Elements of the error matrix S are transformed to an equivalent reduced matrix, during the reduction of A, by computing new values of S_{ij} based on the propagation of errors in the reduction of A. The rank of A is then determined by a direct comparison of the corresponding elements on the principal diagonals of the reduced A and S matrices. The criteria used is that a principal diagonal element of the reduced A matrix is nonzero if its absolute value is equal to or greater than three times the absolute value of the corresponding principal diagonal element of the reduced S matrix. The number of statistically nonzero rows in the reduced A matrix is the rank or the number of independent components in the system. In other words, components are counted only when their contribution to the magnitude of the matrix elements exceeds the experimental error.

Detailed Description of Method

The A matrix is pivoted by an interchange of rows and columns to place the elements whose absolute value is the largest in the 1,1 position. The S matrix is transformed by the same row-column interchanges used in A. The resulting A matrix is then transformed to A' by the operation given by Equation (10) performed on all except the first row.

$$A'_{ij} = A_{ij} - \frac{A_{i1}}{A_{11}} A_{1j} \tag{10}$$

This operation makes all elements in the first column zero except for the first element. The S matrix is transformed to S', according to the theory for the propagation of errors in the elementary operations performed on the A matrix, by the operation given in Equation (11).

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

The reason for pivoting the matrix to place the largest elements on the diagonal is to minimize the rate of propagation of errors. With this arrangement, the coefficients of S^2_{ij}, S^2_{i1}, and S^2_{11} on the right of Equation (11) can never exceed one, and the value of an element in S' after an operation cannot exceed twice the value of the largest of the elements in S that goes into its calculation.

The submatrices formed by deleting the first row and column of A' and S' are then treated similarly to give A" and S". This process is repeated until all the elements of the transformed A matrix below the principal diagonal are equal to zero. It is then only necessary to compare elements on the principal diagonals of the transformed A and S matrices to determine the number of statistically nonzero rows, and, therefore, to find the experimental rank.

Error Matrix S

Early workers in this area (26, 27) assumed a constant error for all A_{ij}. However, Varga and Veatch (31) describe a method for calculating the standard error of the absorbance, S_{ij}, as a function of the photometric error and the measured absorbances, A_{ij}. The relation between relative concentration error, $\Delta C/C$, in a photometric measurement and the photometric error, ΔT, where C is the concentration and T is the transmittance, is given by Equation (12).

$$\frac{\Delta C}{C} = \frac{0.43429\ \Delta T}{T \log T} \tag{12}$$

From this equation and the generalized Beer's law relation, the following expression for the standard error of the absorbance, S_{ij}, can be derived.

$$S_{ij} = 0.43429 \times \Delta T \times \text{antilog } A_{ij} \tag{13}$$

For a given photometric error, ΔT, S_{ij} is a minimum for A_{ij} in the range 0.2 to 0.8 absorbance units. For example, using $\Delta T = 0.005$, $S_{ij} = 1.37\%$ of A_{ij} if $A_{ij} = 0.5$. This approach is much more reasonable than that of assuming a constant error regardless of the size of A_{ij}.

Fortran Program

Wallace and Katz (27) wrote a computer program to perform the rank calculations when large amounts of data were used. This was a Fortran program for an IBM 704 computer. Varga and Veatch (31) modified this program for use on an IBM 7040. A copy of this program was obtained and several changes were made so that the program could be used on the IBM 360.

The most important change was the conversion of the entire program to double precision. Since the program involves a series of row and column operations on rather large matrices, it was necessary to use double precision arithmetic to avoid roundoff error (63). The input statements were changed to make them compatible with the amount of data obtained in this work. All elements, A_{ij} and S_{ij}, below the principal diagonals in the reduced A and S matrices were supposed to be set equal to zero as described in Equations (10) and (11). However, an element occasionally was not set equal to zero in the original program. This was corrected when the other changes were made.

In the original program the elements below the principal diagonal in the last column, the j^{th} column, of the reduced A and S matrices were not set equal to zero. Therefore, the program could not determine the rank of A if the rank was equal to the number of columns j. This was corrected by interchanging the elements in the last column of the reduced A and S matrices to place the maximum elements on the principal diagonals and then setting the elements below the diagonals to zero. The rank of A can now be determined if the rank is less than or equal to the number of columns in the A matrix.

Detailed Description of Program

N, the number of experiments, L, the number of wavelengths, and CRIT, the criterion for setting A elements to zero are read in first. The absorbance data, V(I,J), is read next. Since the program is written in double precision, the next step is to convert the absorbance data to double precision. This yields the absorbance matrix, A(I,J).

The first step in the rank calculation is to calculate the error matrix, S, and write the original A and S matrices. The A and S matrices are then pivoted, reduced, and sub-pivot elements set to zero. This completes the reduction of the two matrices. Then the experimental rank is determined by comparing corresponding elements on the principal diagonals of the A and S matrices. The rank of A(I,J) plus the reduced A and S matrices are written out in the final steps of the program.

The rank calculation is in a DO loop which allows the photometric error to be varied from 0.001 to 0.01 in increments of 0.001. The rank is calculated for each value of the photometric error. By removing the DO statement, the experimental rank can be calculated with a particular photometric error. A flow chart of the program and a listing of the program with a typical data set is given in Appendix A.

CHAPTER IV

SPECIES NUMBER

A graphical method for determining the number of species in solution from spectrophotometric data is described by Coleman, Varga, and Mastin (12). The method is based upon the rank of an absorbance matrix. In this method absorbance data is arranged in matrix form and various functions of the absorbance data are plotted for the cases of one, two, and three absorbing species. For two and three absorbing species, distinction is made between cases in which there are restrictions on the stoichiometry, such as the condition that the sum of the concentrations of the absorbing species is constant, and cases in which there are no restrictions on the stoichiometry. The method is simple to apply when the amount of data is small. However, the calculations and plotting are time consuming for larger amounts of data. Computer methods for handling the data are needed.

Theory

Spectrophotometric measurements provide a powerful means for examining interactions among substances in solution. The information obtained in typical experiments consists of graphs of absorbance A at wavelengths i for a series of solution compositions j. This information can be displayed as a matrix A with elements A_{ij} or in Fortran notation A(I,J). The matrix A is a rectangular array of numbers.

$$A = \begin{bmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{bmatrix} \tag{14}$$

A matrix of i rows and j columns is said to be of order i x j. When i = j, as in matrix A, the matrix is of order j. A determinant can be defined as a square array of numbers that is evaluated according to a certain rule. The order of a determinant is the number of rows (or columns). The largest determinant that can be formed from a square matrix is of the same order as the original matrix as shown in Equation (15).

$$\det[A] = \begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} \tag{15}$$

Other determinants can be formed from the original determinant by deleting an equal number of rows and columns. Nine second order (formed by deleting one row and one column) and nine first order determinants (formed by deleting two rows and two columns) can be obtained from the third order determinant in Equation (15). For example, three second order determinants are:

delete 1st row, 1st column yields $\begin{vmatrix} A_{22} & A_{23} \\ A_{32} & A_{33} \end{vmatrix}$

delete 1st row, 2nd column yields $\begin{vmatrix} A_{21} & A_{23} \\ A_{31} & A_{33} \end{vmatrix}$

delete 1st row, 3rd column yields $\begin{vmatrix} A_{21} & A_{22} \\ A_{31} & A_{32} \end{vmatrix}$

The following theorem will be used in the derivations to follow. Given the points X = (a,b), Y = (c,d), and Z = (e,f) as shown in Figure 1, the value of the determinant, $|D|$, is related to the area of triangle ΔXYZ by Equation (16). The determinants used in the one, two, and three species cases will be shown to be of the above type. The proof of this theorem is given in many standard mathematics texts (64).

$$|D| = \begin{vmatrix} a & b & 1 \\ c & d & 1 \\ e & f & 1 \end{vmatrix}$$

$$|D| = 2 \times \text{AREA } (\Delta XYZ) \qquad (16)$$

One Absorbing Species--No Restrictions on Stoichiometry

If the matrix A is of rank R, where R is the number of independent absorbing species, then each determinant $|A_{ij}|$ of order R+1 must vanish. The value of the transpose of a determinant is the same as the value of the determinant.

$$\begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} = 0 \qquad (17)$$

Taking the transpose of the determinant in Equation (17) yields Equation (18) which can be rewritten as shown in Equation (19).

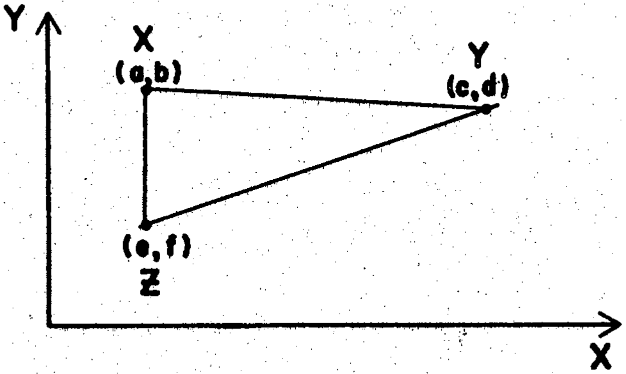


Figure 1. Relationship Between Triangle XYZ and |D|

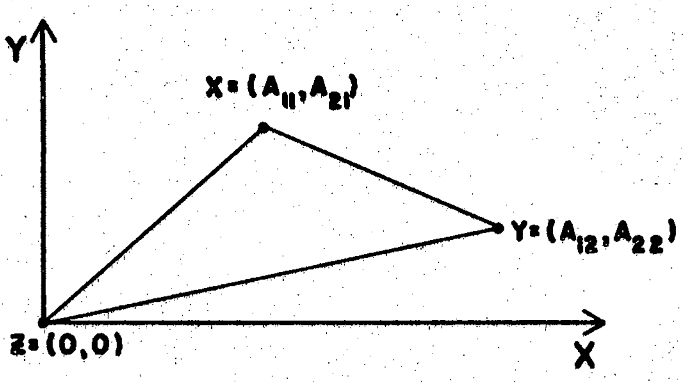


Figure 2. Triangle XYZ for One Absorbing Species

$$\begin{vmatrix} A_{11} & A_{21} \\ A_{12} & A_{22} \end{vmatrix} = 0 \qquad (18)$$

$$\begin{vmatrix} A_{11} & A_{21} & 1 \\ A_{12} & A_{22} & 1 \\ 0 & 0 & 0 \end{vmatrix} = 0 \qquad (19)$$

This is a case of Equation (16) with one set of points at the origin as shown in Figure 2. The value of the determinant must be zero if one species is absorbing, so $|D| = 2 \times \text{AREA}(\Delta XYZ) = 0$. The only way this could be true is for the area of $\Delta XYZ = 0$. This can occur only if points X and Y lie on a straight line through the origin. If the (X,Y) points are plotted, a straight line through the origin for each wavelength pair will be obtained only if one species is absorbing.

$$\begin{array}{c} (A_{11},A_{21}) \\ (A_{12},A_{22}) \\ \vdots \quad \vdots \\ (A_{1j},A_{2j}) \end{array}$$

If more than one species is absorbing, then the value of the determinant in Equation (17) is not necessarily equal to zero and straight lines are not obtained. The absorbance at one wavelength is plotted against the absorbance at each other wavelength. A reference wavelength, usually of maximum absorbance, is used. A series of i straight lines passing through the origin with the number of points on each line equal to the number of solution compositions j is obtained when the data are from a single absorbing species.

Two Absorbing Species--No Restrictions on Stoichiometry

When rank R=2, each determinant of order 3 must vanish.

$$\begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} = 0 \tag{20}$$

To put the determinant in Equation (20) in a form suitable for graphical display, each column is divided by its first element.

$$\begin{vmatrix} 1 & 1 & 1 \\ \dfrac{A_{21}}{A_{11}} & \dfrac{A_{22}}{A_{12}} & \dfrac{A_{23}}{A_{13}} \\ \dfrac{A_{31}}{A_{11}} & \dfrac{A_{32}}{A_{12}} & \dfrac{A_{33}}{A_{13}} \end{vmatrix} = 0 \tag{21}$$

Taking the transpose of Equation (21) yields Equation (22).

$$\begin{vmatrix} 1 & \dfrac{A_{21}}{A_{11}} & \dfrac{A_{31}}{A_{11}} \\ 1 & \dfrac{A_{22}}{A_{12}} & \dfrac{A_{32}}{A_{12}} \\ 1 & \dfrac{A_{23}}{A_{13}} & \dfrac{A_{33}}{A_{13}} \end{vmatrix} = 0 \tag{22}$$

Interchanging columns in Equation (22) yields the form used for plotting. Equation (23) restricts the following (X,Y) points to a straight line because it is of the same form as the determinant in Equation (16).

$$\begin{vmatrix} \dfrac{A_{21}}{A_{11}} & \dfrac{A_{31}}{A_{11}} & 1 \\ \dfrac{A_{22}}{A_{12}} & \dfrac{A_{32}}{A_{12}} & 1 \\ \dfrac{A_{23}}{A_{13}} & \dfrac{A_{33}}{A_{13}} & 1 \end{vmatrix} = 0 \qquad (23)$$

$$X = \left(\frac{A_{21}}{A_{11}}, \frac{A_{31}}{A_{11}}\right)$$

$$Y = \left(\frac{A_{22}}{A_{12}}, \frac{A_{32}}{A_{12}}\right)$$

$$Z = \left(\frac{A_{23}}{A_{13}}, \frac{A_{33}}{A_{13}}\right)$$

Since the value of the determinant equals zero, the area of ΔXYZ in Figure 1 must equal zero. This can occur only if the points X, Y, and Z lie on a straight line. This line will contain points for other solution compositions, $(A_{2j}/A_{1j}\ ,\ A_{3j}/A_{1j})$. Therefore, a plot of absorbance ratios involving three different wavelengths provides a test as to whether a series of spectra can be described in terms of two species.

Three Absorbing Species--No Restrictions on Stoichiometry

When the rank of an absorbance matrix is three, each determinant of order 4 must vanish. Dividing each column of a fourth order determinant by its first element yields Equation (24).

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ \frac{A_{21}}{A_{11}} & \frac{A_{22}}{A_{12}} & \frac{A_{23}}{A_{13}} & \frac{A_{24}}{A_{14}} \\ \frac{A_{31}}{A_{11}} & \frac{A_{32}}{A_{12}} & \frac{A_{33}}{A_{13}} & \frac{A_{34}}{A_{14}} \\ \frac{A_{41}}{A_{11}} & \frac{A_{42}}{A_{12}} & \frac{A_{43}}{A_{13}} & \frac{A_{44}}{A_{14}} \end{vmatrix} = 0 \qquad (24)$$

Subtracting the first column from each of the other columns, expanding along the first row, and dividing each row by its last element yields Equation (25). The general form is given in Equation (26).

$$\begin{vmatrix} \frac{A_{11}A_{22}-A_{12}A_{21}}{A_{11}A_{24}-A_{14}A_{21}} \times \frac{A_{14}}{A_{12}} & \frac{A_{11}A_{23}-A_{13}A_{21}}{A_{11}A_{24}-A_{14}A_{21}} \times \frac{A_{14}}{A_{13}} & 1 \\ \frac{A_{11}A_{32}-A_{12}A_{31}}{A_{11}A_{34}-A_{14}A_{31}} \times \frac{A_{14}}{A_{12}} & \frac{A_{11}A_{33}-A_{13}A_{31}}{A_{11}A_{34}-A_{14}A_{31}} \times \frac{A_{14}}{A_{13}} & 1 \\ \frac{A_{11}A_{42}-A_{12}A_{41}}{A_{11}A_{44}-A_{14}A_{41}} \times \frac{A_{14}}{A_{12}} & \frac{A_{11}A_{43}-A_{13}A_{41}}{A_{11}A_{44}-A_{14}A_{41}} \times \frac{A_{14}}{A_{13}} & 1 \end{vmatrix} = 0 \qquad (25)$$

$$\begin{vmatrix} X_1 & Y_1 & 1 \\ X_2 & Y_2 & 1 \\ X_3 & Y_3 & 1 \end{vmatrix} = 0 \qquad (26)$$

Using Equation (16) again, it is seen that if a system contains three absorbing species a family of straight lines is obtained. The number of lines obtained is j, the number of solution compositions, with i points on each line. Since all values of X contain the term A_{14}/A_{12} and all values of Y contain the term A_{14}/A_{13}, the simplified elements of the determinant given in Equation (27) will also give linear plots which differ only in slope from the plots obtained using Equation (25).

$$\begin{vmatrix} \dfrac{A_{11}A_{22}-A_{12}A_{21}}{A_{11}A_{24}-A_{14}A_{21}} & \dfrac{A_{11}A_{23}-A_{13}A_{21}}{A_{11}A_{24}-A_{14}A_{21}} & 1 \\ \dfrac{A_{11}A_{32}-A_{12}A_{31}}{A_{11}A_{34}-A_{14}A_{31}} & \dfrac{A_{11}A_{33}-A_{13}A_{31}}{A_{11}A_{34}-A_{14}A_{31}} & 1 \\ \dfrac{A_{11}A_{42}-A_{12}A_{41}}{A_{11}A_{44}-A_{14}A_{41}} & \dfrac{A_{11}A_{43}-A_{13}A_{41}}{A_{11}A_{44}-A_{14}A_{41}} & 1 \end{vmatrix} = 0 \qquad (27)$$

Since there may be many possible wavelength combinations if data are available at a large number of wavelengths, the number of combinations chosen for graphical display is usually limited as follows: (a) for one species, values of A_{mj} versus A_{ij}, $i \neq m$, are plotted where m is a wavelength of maximum absorbance; (b) for two species, A_{mj}/A_{nj} versus A_{ij}/A_{nj}, $i \neq m$ or n, are plotted where m is defined as above and n is any other wavelength; (c) for three species, $(A_{mx}A_{iy}-A_{my}A_{ix})/$

$(A_{mx}A_{iz}-A_{mz}A_{ix})$ versus $(A_{mx}A_{ij}-A_{mj}A_{ix})/(A_{mx}A_{iz}-A_{mz}A_{ix})$, $i \neq m$, $j \neq x$, y, or z are plotted, where m is defined as above and x, y, and z are three arbitrary (but fixed) solution compositions.

Two Absorbing Species--Restrictions on Stoichiometry

Up to this point no restrictions have been imposed upon solution compositions. The results for one, two, and three absorbing species are general but for certain cases interpretation is easier when there are restrictions on the stoichiometry.

Spectra of metal complexes are often reported for a series of solutions prepared by varying the ligand concentration at constant stoichiometric concentration of the metal ion such that the sum of the concentrations of the absorbing species is equal to a constant. Consider a series of complex ions, ML_n, where $n = 0$ to N. Let $\sum_{n=0}^{N} ML_n$ equal the constant stoichiometric concentration. Assume that the concentrations of two absorbing species are related as shown in Equation (28).

$$[I] + [II] = C \tag{28}$$

If the path length is one centimeter, the absorbance is given by Equation (29).

$$\begin{aligned} A &= \epsilon_I\ [I] + \epsilon_{II}\ [II] \\ &= \epsilon_I(C - [II]) + \epsilon_{II}\ [II] \\ &= \epsilon_I C + (\epsilon_{II} - \epsilon_I)\ [II] \end{aligned} \tag{29}$$

Using Fortran notation, the absorbance at wavelength λ_1 in solutions J and JB, where J is any solution and JB is a reference solution, is given by Equations (30) and (31). Similar equations can be written for wavelength λ_m and solutions J and JB. Subtracting Equation (31) from Equation (30) and Equation (33) from Equation (32) yields Equations (34) and (35), which give upon division the final form used for plotting.

$$A(\lambda_1,J) = \epsilon_I^{\lambda_1} C + (\epsilon_{II}^{\lambda_1} - \epsilon_I^{\lambda_1}) \; [II]_J \tag{30}$$

$$A(\lambda_1,JB) = \epsilon_I^{\lambda_1} C + (\epsilon_{II}^{\lambda_1} - \epsilon_I^{\lambda_1}) \; [II]_{JB} \tag{31}$$

$$A(\lambda_m,J) = \epsilon_I^{\lambda_m} C + (\epsilon_{II}^{\lambda_m} - \epsilon_I^{\lambda_m}) \; [II]_J \tag{32}$$

$$A(\lambda_m,JB) = \epsilon_I^{\lambda_m} C + (\epsilon_{II}^{\lambda_m} - \epsilon_I^{\lambda_m}) \; [II]_{JB} \tag{33}$$

$$A(\lambda_1,J) - A(\lambda_1,JB) = (\epsilon_{II}^{\lambda_1} - \epsilon_I^{\lambda_1})([II]_J - [II]_{JB}) \tag{34}$$

$$A(\lambda_m,J) - A(\lambda_m,JB) = (\epsilon_{II}^{\lambda_m} - \epsilon_I^{\lambda_m})([II]_J - [II]_{JB}) \tag{35}$$

$$A(\lambda_1,J) - A(\lambda_1,JB) = \frac{\left(\epsilon_{II}^{\lambda_1} - \epsilon_I^{\lambda_1}\right)}{\left(\epsilon_{II}^{\lambda_m} - \epsilon_I^{\lambda_m}\right)} (A(\lambda_m,J) - A(\lambda_m,JB)) \tag{36}$$

A plot of $A(\lambda_1,J) - A(\lambda_1,JB)$ at λ_1 versus the corresponding differences at other wavelengths yields a straight line through the origin with the number of points on each line equal to the number of solution compositions J. The number of wavelength pairs determines the number of lines obtained. This is the same form as the case of one species absorbing with no restrictions on the stoichiometry.

Three Absorbing Species--Restrictions on Stoichiometry

In a closed system, the total concentration of the several components remains constant. Therefore, P in Equation (9) is equal to one. If a system contains three absorbing species, the sum of whose concentrations is a constant, then the rank R should equal two. A derivation similar to that shown for two absorbing species with restrictions on the stoichiometry yields equations which reduce to the same form as the two species case without restrictions. I straight lines, not through the origin, with J points on each line are obtained from a system containing three absorbing species if the following (X,Y) points are plotted.

$$\frac{A(LM2,J) - A(LM2,JB)}{A(LM1,J) - A(LM1,JB)} \quad \text{versus} \quad \frac{A(I,J) - A(I,JB)}{A(LM1,J) - A(LM1,JB)} \qquad (37)$$

LM1 and LM2 are two arbitrary (but fixed) reference wavelengths and JB is a reference solution.

Species Number Program

In typical experiments it is useful to explore many more possible combinations of absorbance data than is feasible by desk calculation. Also, the graphical methods give no objective measure of the linearity of the functions plotted. Therefore, a computer program was written to test each data set for linearity assuming one, two, and three absorbing species for either constant or nonconstant stoichiometry. This program fits the best least squares straight line through each data set, calculates the intercept and slope of each line, gives a measure of the goodness-of-fit, and plots both the experimental and calculated lines for each case. The absorbance data plus various control parameters, which determine the model to be used, are the only input data required. Several examples using this program are given in a recent paper (12).

General Description of Program

The program is written in Fortran IV and was originally used on an IBM 7040. The entire program was converted to double precision for use on an IBM 360. The program consists of a main program and three subroutines. The main program reads in the absorbance data, calculates the (X,Y) functions to be plotted, performs a least squares curve fit on these data, and prints out the experimental data plus the calculated quantities, such as the slope and intercept of the best straight line through the data, the standard deviation of each point, and the goodness-of-fit parameter. The subroutines are a plot routine which plots the experimental and calculated curves, a small subroutine called by the plot subprogram to perform certain calculations, and a matrix inversion routine called by the main program during the least squares calculation.

Detailed Description of Program

All elements of each array are set equal to zero first. Then MSIZE, the maximum size polynomial which can be used in the least squares curve fitting procedure, SIZE, the size polynomial to be used, and NCONT, the number of models or polynomials to be tried are read next. The values of CONTL, which determine if the coefficients of the polynomials are to be fixed or calculated, are read in next. The initial values of the BETAS are then read in as zeros. The heading for the output table, HEAD, the title for the plot, TITLE, the ordinate label, MOP, the abscissa label, TAB1, the symbols to be used on the plot, NCH, and the name of the system being studied are the next data input. MM, the number of solution compositions or experiments, L, the number of wavelengths, LM, LM1, LM2, wavelengths of maximum absorbance, JB, JB1, JB2, reference solutions, and NSTOIC, a parameter which is one if nonconstant stoichiometry is assumed or zero for constant stoichiometry, are read in next. ITER and IT1 are parameters which determine which number of species case is to be tried. After the error parameter, DELT, is read, the final data input is the absorbance array, C(I,J).

The absorbance data is converted to double precision and stored in A(I,J). ITER is initially one, two, or three. If ITER is one, Equation (19) is used to calculate XA(LM,J) and YA(I,J) for the one absorbing species case. If ITER equals two and NSTOIC is one, Equation (23) is used to calculate (X,Y) points for two absorbing species with no restrictions on the stoichiometry. However, if ITER is two and NSTOIC is zero, Equation (36) is used for two species with restrictions on the stoichiometry. If ITER is three and NSTOIC is one, Equation (27) is used for three species with no restrictions on the stoichiometry. If ITER is three and NSTOIC is zero, Equation (37) is used to calculate (X,Y) points for three absorbing species with restrictions on the stoichiometry. After each of these cases, the program branchs around the other cases. IF statements at the end of the program allow a return to this part of the program to try each case in turn if desired.

The next step in the program is to calculate XMIN and XMAX for the plot routine. After this, the best least squares straight line is calculated for the experimental (X,Y) data. The values of the BETAS, coefficients of the polynomial fit, and their standard deviations, DEV, are calculated and written out. SMIN, the goodness-of-fit parameter, is calculated next. SMIN is defined as the sum of the weighted squares of the deviations, S, divided by the degrees of freedom, DF.

The heading for the output table, the experimental (X,Y) points, weight of the data, calculated Y (YHAT), DEV, S, and SMIN are written out. YMIN and YMAX for the plot are then calculated. Since all calculations were performed in double precision, the next step is to convert all the data to single precision before the experimental and calculated (X,Y) points are plotted. This least squares curve fitting procedure followed by the plot routine is repeated for each wavelength for a particular number of absorbing species.

For example, assume an unknown system contains either one or two absorbing species with no restrictions on the stoichiometry. XA and YA functions are calculated for each wavelength and solution composition using Equation (19). Then, at each wavelength the best straight line through the points is calculated and the experimental and calculated curves are plotted. The program then returns and calculates new XA and YA functions at each wavelength using Equation (23). The least squares curve fit and plotting procedure is repeated at each wavelength. In most cases, the best model (one or two absorbing species) can be determined by visual inspection of the curves for each wavelength. If not, a comparison of the goodness-of-fit parameters yields the best fit. A flow chart and listing of this program plus a typical data set is given in Appendix B.

CHAPTER V

CORRESPONDING SOLUTIONS

It is difficult to interpret measurements of A and [L] unambiguously, except in the simplest cases. Graphical methods described earlier can be used for $N = 1$ and in some cases for $N = 2$ if one or more extinction coefficients can be determined independently. Although the values of β_n and ϵ_n may be refined by successive approximation, considerable uncertainty often exists in constants obtained by extrapolation methods. More satisfactory values can be obtained in cases where it is possible to calculate $\bar{n}$, [L] values from spectrophotometric data.

Method of Corresponding Solutions

Rearranging Equation (4) gives Equation (38).

$$C_L = \bar{n}C_M + [L] \tag{38}$$

For a series of "corresponding" solutions having the same (unknown) values of $\bar{n}$ and [L] but containing different total concentrations of M and L, a plot of C_L versus C_M should be a straight line of slope $\bar{n}$ and intercept [L] (25). The correspondence between two or more solutions can be established using any property that is a function of the free ligand concentration only. This method can be used only for systems in which $C_L - [L]$ differs appreciably from both C_L and zero. The corresponding solution function, E, is defined in Equation (39), where A is the absorbance, 1 is the path length, ϵ_L is the extinction coefficient of the ligand, and C_L,C_M are the total ligand and total metal concentrations.

$$E = \frac{A-1\epsilon_L C_L}{1C_M} \tag{39}$$

Substitution of Equations (2), (3), and (6) in Equation (39) yields the following expression which shows that E is a function of the free ligand concentration only.

$$E = \frac{\Sigma(\epsilon_n - n\epsilon_L)\beta_n[L]^n}{\beta_n[L]^n} = f([L]) \tag{40}$$

If the value of E is the same throughout a series of solutions which contain different total concentrations of M and L, the value of [L] must also be the same, provided that only mononuclear complexes are formed (25).

The experimental procedure is to measure the absorbance of a series of solutions containing different total concentrations of M and L. E is then calculated according to Equation (39). Plots of E versus C_L for each C_M, as shown in Figure 3, are interpolated at chosen E values to obtain pairs of values of C_L and C_M for corresponding solutions. Then linear plots of C_L versus C_M are made (Figure 4) and values of $\bar{n}$ and [L] are obtained from the slope and intercept of each line.

One serious limitation of this method is that it cannot be used if polynuclear complexes exist in solution. From the relation $C_L = [L] + \bar{n}C_M$, $\bar{n}$ is given by Equation (41).

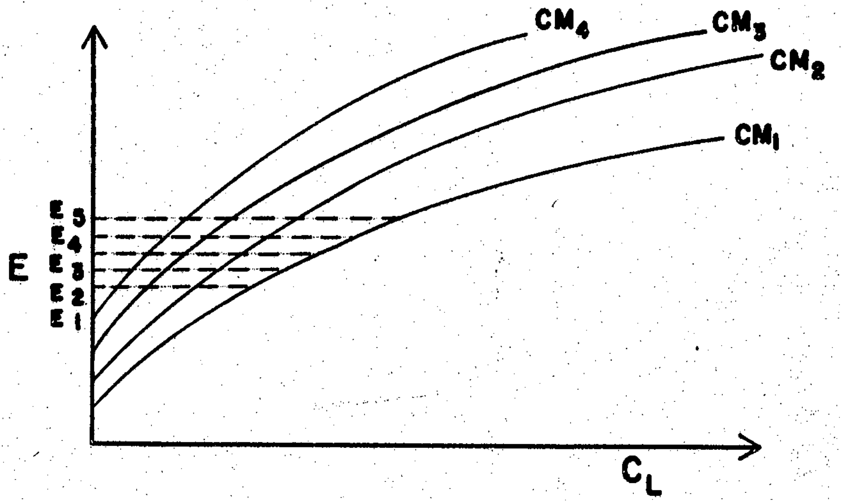


Figure 3. Corresponding Solutions Function E Versus C_L at Constant C_M

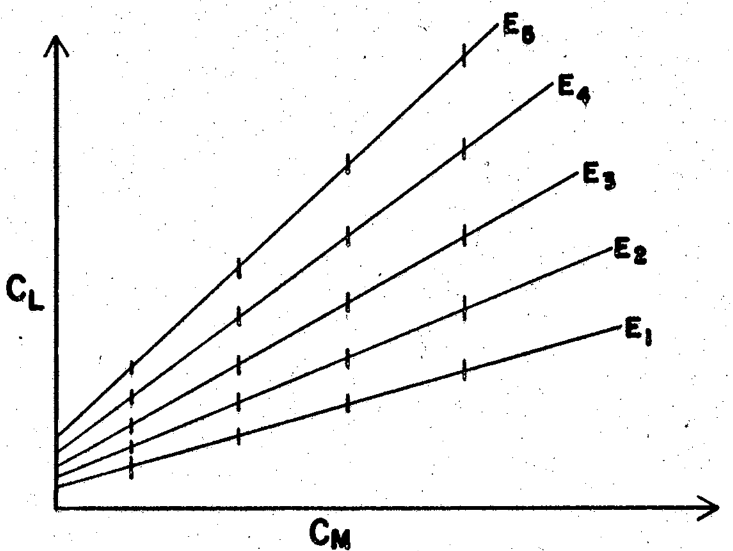


Figure 4. Plot of C_L Versus C_M for Determining $\bar{n}$,[L] Values

$$\left(\frac{\partial C_L}{\partial C_M}\right)_E = \bar{n} \tag{41}$$

When dinuclear or higher polynuclear complexes are present in solution, the expression for $(\partial C_L/\partial C_M)_E$ contains [M] and the extinction coefficients of the different complexes. Therefore, the derivative depends on C_M and at a constant value of the intercept on the C_L axis, the calculated value of $\bar{n}$ depends on the wavelength used (65). At $C_M = 0$, the derivative is made up of the real ligand number $\bar{n}$ and a term depending on the wavelength. In general, $\bar{n}$ is a function not only of [L] but also C_M if polynuclear complexes are present. Therefore, corresponding values of C_L,C_M will not necessarily fall on a straight line.

To check for the presence of polynuclear species, measurements should be made at several wavelengths, preferably in different absorption bands. If only mononuclear complexes are present, the same result will be obtained at each wavelength. However, different $\bar{n}$, [L] curves will be obtained at different wavelengths if polynuclear species are present.

Computer Programs

Two computer programs have been written to analyze spectrophotometric data obtained using the method of corresponding solutions. The first program calculates the corresponding solution functions, E, for each C_L and C_M and plots E versus C_L at constant C_M for all wavelengths. The values of E, C_L, and C_M are written out for each wavelength. This program will be referred to as the corresponding solution plot program. The second program, referred to as the corresponding solution $\bar{n}$,[L] program, uses the E values calculated in the plot program plus other experimental data to calculate $\bar{n}$,[L] values by the method shown in Figures 3 and 4.

Corresponding Solution Plot Program

This program was written in Fortran IV and uses single precision arithmetic. Since no matrix operations are needed, double precision arithmetic was not necessary. The programs were run on an IBM 360.

The input data are sets of absorbance readings obtained from measurements on series of solutions containing varying concentrations of metal and ligand. C_L and C_M values, plus extinction coefficients, ε_L, of the ligand at each wavelength are also read in at the start of the program. Using all combinations of C_L and C_M, these data are used to calculate the corresponding solution functions, E, as given in Equation (39). The calculated E values along with the corresponding values of C_L, C_M and ε_L are written out at each wavelength. The program as written can handle up to seven C_L concentrations and 80 wavelengths. The number of C_L concentrations and wavelengths can be increased by simply changing a dimension statement and reading in the data. The maximum number of C_M concentrations is determined by the number of curves which the plot routine can accept. This is considerably larger than the number of C_M concentrations usually used in studies of metal complexes. The program is written for the case of four C_M concentrations.

After the above data is written out for each wavelength, a plot of E versus C_L at constant C_M is made at each wavelength. The number of curves on each plot is equal to the number of C_M values with the number of points on each curve equal to the number of C_L concentrations. These plots are used to select E values for the interpolation described earlier. It is obvious from Figure 3 that use of E values greater than E_5 will produce large errors in the calculated C_L values because the E versus C_L curves are approximately horizontal. Therefore, the plots are inspected at each wavelength of interest to choose a range of E values for which the slopes of the curves are significant. A flow chart, program listing, and typical data set is given in Appendix C.

Corresponding Solution $\bar{n}$,[L] Program

The method of corresponding solutions is an excellent method for studying complex equilibria in solution. This method yields $\bar{n}$,[L] data from which stability constants can be obtained. However, the calculations, plotting, and interpolation become cumbersome when large amounts of data are available. Also, the graphical procedure gives no measure of the linearity of C_L versus C_M plots which are used to calculate $\bar{n}$,[L] values. In order to speed up and improve the accuracy of the method, a computer program was written to perform the necessary calculations.

General Description of Program

The program was written in Fortran IV for use on an IBM 360. Since matrix calculations were involved, the program was written in double precision. The experimental data input for the program are the E functions at a particular wavelength plus C_L and C_M concentrations. Using a least squares curve fitting procedure, the best fit for each of the E versus C_L at constant C_M curves is calculated. These curves are then interpolated at chosen E values and corresponding values of C_L and C_M are calculated. Then the best straight line is fitted to each set of C_L,C_M values and the slope ($\bar{n}$) and intercept ([L]) are calculated for each. The coefficients for the polynomial fits of the E versus C_L curves as well as the straight line fits of C_L,C_M data sets are written out along with their standard deviations. Plots of experimental and calculated C_L,C_M curves can be made if desired.

Detailed Description of Program

The first control parameter specified is NC. This parameter can have values of zero or one depending upon the part of the program being executed. The least squares curve fitting procedure is used in two parts of the program. It is first used to calculate the best polynomial fit of E versus C_L curves. NC equals zero for this part of the program. After the interpolation section, the least squares procedure is used again to fit the C_L,C_M data sets. For this part of the program, NC is one.

After NC is set to zero, the headings for the output table, HEAD, the title for the plot, TITLE, the X and Y coordinate labels, TAB1 and MOP, the symbols for the plot, NCH, and the name of the system being studied are read in. L, the number of C_M concentrations, MMM, the number of E values, MSIZE, the maximum size polynomial which can be used to fit the data, NCONT, the number of polynomial models to be tried, and MPT, the maximum number of C_L points at any given C_M are read in next. MM, the number of C_L values at each C_M, XA and YA arrays, the C_L and E functions for E versus C_L plots, and CONTL, the parameter which determines the particular polynomial model to be used, are read in at one time if MPT $\leq$ 8. A 7th degree polynomial is the maximum size which can be used. Therefore, up to and including 8 points per curve can be fit exactly with a particular model. For example, if there are 7 C_L

concentrations for a given C_M, a 6th degree polynomial will fit the data exactly. For this reason only one model need be tried for MPT ≤ 8 and CONTL is read in at the same time as the X,Y points (statement 114).

However, if MPT ≥ 9, all possible polynomials (through 7th degree) must be tried in order to be sure of obtaining the best possible fit. Each of the 127 possible models must be tried and a control card (CONTL) read in for each. Therefore, all CONTL cards are read in at the start of the program (statement 110). The other experimental data is read in as described earlier.

The next step of the program is to calculate XMIN, XMAX for the plot. After the minimum and maximum values of the X coordinates have been calculated, the least squares curve fitting procedure is used to calculate the best fit for each experimental curve (E versus C_L at constant C_M). One model or many may be tried for each C_M. The values of the BETA's, coefficients of the polynomial fit, and their standard deviations, DEV, are calculated for each model. The goodness-of-fit parameter, SMIN, is calculated for each also. SMIN is the sum of the weighted squares of the deviations from the experimental data divided by the degrees of freedom. If the standard deviation of a BETA for a particular model is greater than the absolute value of the BETA itself, this model is discarded. When a model satisfies this criteria, the SMIN's for successive models are compared. The best fit of the data is the model whose BETA's are greater than their standard deviations and whose SMIN is the smallest. This procedure is repeated for each E versus C_L curve.

The BETA's, their standard deviations, and SMIN are written out for each model for each C_M. Then, after all models have been tried, the best fit values of BETA, standard deviations, and SMIN are written out. The BETA's for the best fit are stored in the BB array for use in the interpolation procedure. This describes what occurs through statement 116.

The E values for the interpolation as shown in Figure 3 are read in next. The interpolation procedure is quite simple although it would be very time consuming without use of a computer. An expression involving the BETA's from the best fit for each C_M and the C_L values is set up as shown in Equation (42).

$$\mathrm{SUM} = \mathrm{BB}(I,1) + \mathrm{BB}(I,2) \times C_L + \mathrm{BB}(I,3) \times C_L^2 + \text{-----} \mathrm{BB}(I,8) \times C_L^7 \qquad (42)$$

Using the first E value, C_L is initialized to some value (arbitrary) between 0 and 100 (C_L and C_M concentrations are scaled before input). This value of C_L is substituted in Equation (42) and the value of SUM is calculated. SUM and E are compared by using a set of IF statements and by incrementing C_L the difference between SUM and E is made less than or equal to 1.0×10^{-4}. This procedure is repeated for each C_M. Then a new E value is used and the whole process is repeated for each C_M. The result is a set of corresponding C_L, C_M values for each E.

The final step of the program is to go back to the least squares curve fitting routine and fit the best straight line through each C_L, C_M set. The slope and intercept and their standard deviations are printed out along with SMIN for each line. Since the input data have been scaled, the [L] has to be multiplied by the scaling factor. The experimental and calculated curves can be plotted if desired by simply adding a plot subroutine and a CALL statement.

The results obtained from this program are a set of $\bar{n}$,[L] values for input to a formation function program which calculates the stability constants relating the species in solution. This program was checked using several sets of literature data. The first set of data used was Ahrland's (66) data on the uranyl ion. Six C_L concentrations for each of three C_M concentrations were used and the curves were interpolated at six E values. The following results were obtained using a fifth degree polynomial to fit the six experimental points for each C_M.

TABLE I

COMPARISON OF GRAPHICAL AND COMPUTER METHODS I

	Ahrland's Graphical Method		This Program	
E	$\bar{n}$	[L]	$\bar{n}$	[L]
105	0.47	12.1	0.51	10.86
130	0.71	22.9	0.69	23.17
160	0.97	45.2	1.00	44.98
190	1.33	91.6	1.33	91.70
205	1.57	139.6	1.46	140.38
210	-	-	1.98	158.70

A similar comparison was made using Fronaeus (67) work on nickel thiocyanate complexes. The results are shown in Table II. In this case, MPT was greater than 8, so 127 possible models were tried as described earlier. The best fit was then used for interpolation and the calculation of $\bar{n}$,[L] values. A flow chart, program listing and a typical data set is given in Appendix D.

TABLE II

COMPARISON OF GRAPHICAL AND COMPUTER METHODS II

	Fronaeus Graphical Method		This Program	
E	$\bar{n}$	[L]	$\bar{n}$	[L]
5	0.53	42.0	0.51	42.5
7	0.65	61.0	0.64	60.8
10	0.86	87.5	0.83	88.1
15	1.06	137.0	1.07	136.6
20	1.28	187.0	1.26	187.8
25	1.42	240.0	1.41	240.4
30	1.48	297.0	1.50	296.3
35	1.54	355.0	1.54	354.7
40	1.56	414.0	1.58	413.5

Formation Function Program

The final step in the computer analysis of spectrophotometric data obtained using the method of corresponding solutions is to calculate the stability constants of the mononuclear complexes from $\bar{n}$,[L] data. A least squares curve fitting and plotting routine written by Varga (1) is used. The program is written in Fortran IV for use on an IBM 360. All matrix algebra is done in double precision.

The basis of the program is a functional model of the system which is linear in the unknown coefficients. An expression of the form given in Equation (43) is used.

$$Y = a_0 + a_1X + a_2X^2 + - - - + a_NX^N \qquad (43)$$

The average number of bound ligands per central metal ion, $\bar{n}$, can be expressed as a function of the free ligand concentration and the unknown stability constants.

$$\bar{n} = \frac{C_L - [L]}{C_M} = \frac{\beta_1[L] + 2\beta_2[L]^2 + --- + N\beta_N[L]^N}{1 + \beta_1[L] + \beta_2[L]^2 + --- + \beta_N[L]^N} \qquad (44)$$

Rearranging Equation (44), an expression of the form of Equation (43) is obtained where $\beta_0 = 1$.

$$(\bar{n} - 0)\beta_0[L] + (\bar{n} - 1)\beta_1[L] + --- + (\bar{n} - N)\beta_N[L]^N = 0 \qquad (45)$$

The input data are a set of average ligand numbers, $\bar{n}$, and corresponding free ligand concentrations, $[L]$, and an error parameter. The program calculates the over-all formation constants, β_N, standard deviations, SIGMA, and an estimate of the goodness-of-fit, SMIN, for up to 63 possible combinations of N from 1 to 6 in the polynomial $\Sigma(\bar{n} - N)\beta_N[L]^N = 0$, where N ranges from 0 to 6 and $\beta_0 = 1.0$. The β_N and (β_N - SIGMA) must be positive and SMIN/(DF-1) must be 1.5 or less. DF is the number of degrees of freedom. The maximum size of the model may be decreased and the β's may be given fixed values. If data point error parameters are not available, an option in the program allows an unweighted least squares calculation of an error set which is then included in the weighted least squares calculation of the unknown coefficients. The output consists of the stability constants and their standard deviations plus the experimental and calculated $\bar{n}$ values. The goodness-of-fit parameter is printed out also. The experimental and calculated formation function, $\bar{n}$ versus $[L]$, are plotted to allow a direct comparison between parametric and graphical measures of goodness-of-fit. A detailed description of the program has been published and program flow charts and listings are available (1).

CHAPTER VI

PIT-MAPPING

The interpretation of spectrophotometric data obtained from a system containing mononuclear, polynuclear, or a mixture of mononuclear and polynuclear species is quite difficult. Since the functional relationship between the unknown parameters is nonlinear, the general trend has been to use the Gauss method of linearization of a nonlinear relationship. Sillen (37) has recently published a series of papers describing a general least squares method which is valid for nonlinear functions. These are hard to treat by the standard methods for linear functions or the Gauss approximation method. Sillen's programs were written in Algol. A Fortran version of this programming method was used by Metzler (42) and this program was modified by Thomson (68). A copy of Thomson's program was obtained and after a few changes was used in this work.

Theory of Pit-Mapping

The problem of determining the equilibrium constants for a number of simultaneous equilibria in solution can be expressed as a special case of the following general problem. A functional relationship, f, between a measured quantity, y, and some accurately known experimental quantities a_1, a_2, --- is assumed where k_1, k_2, ---, k_N are unknown constants.

$$y = f(k_1, k_2, \text{---}, k_N; a_1, a_2, \text{---}) \tag{46}$$

If (a) the expression for f is correct, (b) there are no errors except the random errors in y, (c) the errors in y are normally distributed around the correct value, and (d) the weight w_i given to each measurement y_i is inversely proportional to the square of its standard deviation, then the "best" values for $k_1, k_2, \text{---}, k_N$ are those that minimize the error-square sum, U.

$$U = \sum_i w_i(y_i - f(k_1, k_2, \text{---}, k_N; a_{1i}, a_{2i}, \text{---}))^2 \tag{47}$$

If f is a linear function of the k's, the least squares condition leads to linear equations which can be solved by straightforward methods. If f is not a linear function of the k's, the general trend has been to reduce it to a linear one by an approximation such as expressing the derivatives of U as a Taylor series and then using only the first terms (Gauss Method).

Pit-mapping does away with the condition that the equations should be linear by considering directly the error-square sum as a function of the unknown k's as given in Equation (48).

$$U(k_1, k_2, \text{---}, k_N) \tag{48}$$

It is assumed in nonlinear cases that the area surrounding the minimum value of the error-square sum, known as the "pit", is described by a second-degree surface. By varying systematically the values for N unknown constants, ½(N + 1)(N + 2) points are obtained which define the surface of the error function. This surface is a generalized elliptic paraboloid in (N + 1)-dimensional space and the coordinates, the unknown constants, corresponding to the lowest point on the error function surface can be directly calculated.

The method of variation and refinement of the equilibrium constants has been summarized in matrix notation (38). The variation technique, called a "shot", can be summarized by Equation (49) where k and c are column matrices (vectors) with N elements, $|k_1\ k_2\ \ldots\ k_N|$ and $|c_1\ c_2\ \ldots\ c_N|$.

$$k = c + SHv \tag{49}$$

c is the current set of trial equilibrium constants and k is the column vector of the new approximations to the constants. H is a diagonal step matrix which controls the magnitude of the variation and S is a trigonal twist matrix which defines the direction in which to vary the vector k. If the "pit" (minimum in U) is skew, that is its main axes are at angles to the coordinate axes k_i, the speed and accuracy of the program is improved by varying k along this main axis instead of parallel to the coordinate axes. The twist matrix S performs this operation. v is a variation vector chosen so that during the shot all elements are zero except one or two at a time that are +1 or −1. In other words, a maximum of two constants are varied simultaneously.

In the program, S and H are treated as a single square matrix, SH.

$$SH = \begin{bmatrix} h_1 & s_{12} & --- & s_{1N} \\ 0 & h_2 & --- & s_{2N} \\ \vdots & \vdots & & \vdots \\ 0 & 0 & --- & h_N \end{bmatrix} \tag{50}$$

Initially, the elements, h_i, are given the user supplied value DEC (0.05 to 0.1 in this work) and all elements s_{ij} are set to zero. As information on the shape of the "pit" is accumulated, the elements of SH are improved using a trigonal correcting matrix, W. The elements of W depend on the shape of the "pit". The amount by which each constant is varied is not the same for all constants and as successive approximations give current constants with error-square sums further down in the "pit", the direction and amount to vary each constant is determined by the shape of the "pit".

The equation of the second-degree surface of the error function can be expressed as shown in Equation (51) where U_c is the value at the central point (k = c, v = 0), p is a vector, and R is a matrix.

$$U = U_c - 2pv + vRv \tag{51}$$

Using all values of the variation vector, ½(N + 1)(N + 2) values of U are calculated. These U values are then used to calculate the terms in p and R as described by Sillen (38). The variation vector, v_0, to obtain the constants at the minimum, k_0, is found from Equation (52).

$$v_0 = pR^{-1} \tag{52}$$

Using v_0, the vector k_0 at the calculated minimum point can be found using Equation (53).

$$k_0 = c + SHv_0 \tag{53}$$

The value of the error-square sum at the minimum, U_0, is then calculated using Equation (54).

$$U_0 = U_c - pv_0 \tag{54}$$

If the calculated U_0 is lower than earlier U values, it is accepted as the new central value and the whole process repeated until there is no change between successive U's.

Application of Pit-Mapping to Spectrophotometric Data

Assuming that Beer's law applies for each of the J species in solution, an observed absorbance A can be represented by

$$A = \sum_{j=1}^{J} C_j \epsilon_j 1 \tag{55}$$

where C_j is the concentration and ϵ_j is the molar extinction coefficient of the j^{th} species in solution. The path length, 1, is one centimeter. The error-square sum, U, is then defined as shown in Equation (56) where i is the solution number and k is the wavelength.

$$U = \sum_{ik} w_k (A_{ik} - \sum_{j=1}^{J} C_{ji} \epsilon_{jk})^2 \tag{56}$$

In this work the weighting factor, w_i, for all data was unity. The error-square sum is minimized when $\partial U / \partial \epsilon_{jk} = 0$ resulting in J simultaneous equations at each wavelength, k.

$$\sum_{j=1}^{J} \left(\sum_i C_{ji} C_{j'i} \right) \epsilon_{jk} = \sum_i C_{j'i} A_{ik} \tag{57}$$

In this version of the pit-mapping program j' = 1, 2, 3, and 4, since a maximum of four species with unknown molar extinction coefficients are considered in subroutine ECOEF. Equation (57) is solved for the molar extinction coefficients by the standard method of Cramer's Rule. The solution of Equation (57) can be written as the ratio of two determinants where $D = (\sum_i C_{ji} C_{j'i})$; j, j' = 1, 2, 3, and 4, and D_{jk} is the matrix in which the j^{th} column of D is replaced by the vector given in Equation (59).

$$\epsilon_{jk} = |D_{jk}| / |D| \tag{58}$$

$$\left(\sum_i C_{1i} A_{ik}, \sum_i C_{2i} A_{ik}, \sum_i C_{3i} A_{ik}, \sum_i C_{4i} A_{ik} \right) \tag{59}$$

Using these values of the molar extinction coefficients and the concentrations of the species, the error-square sum can be calculated from Equation (56). The concentrations of the species in solution are calculated in subroutine EQUIL, from initial approximations to the equilibrium constants and an assumed model of the system. The EQUIL subroutine must be rewritten for each different model of the system. Complete details will be given in a later section.

Pit-Mapping Program

The computer program consists of a main program with ten subroutines and two function subprograms. A listing of the program with a typical data set is given in Appendix E. A detailed flow chart is given elsewhere (68). The input data required are a set of absorbance readings, total ligand and total metal concentrations, solution pH's, trial stability constants, known molar extinction coefficients, and various control parameters. The modifications of the main program and the EQUIL subroutines used in this work will be described in detail. A brief summary of the primary functions of the other parts of the program will be given. A detailed description is given elsewhere.

The primary function of the main program, MAIN, is to read input data and print out the final results. It also contains the IF statements to check for negative constants as well as other convergence criteria. As the k_0 are calculated, each constant is checked to determine if the program has moved it to a negative value. If so, a "dummy" subroutine (MIKO) is entered and the program stops. The variation vector, v_0, needed to calculate the constants at the minimum and the actual k_0 set are calculated in MAIN. The standard deviations of these constants are also calculated.

The modifications of MAIN were in the input and output sections. The program as now written prints out the trial stability constants plus the total ligand and metal concentrations. Then the absorbance data is printed out. The "best" set of constants plus their standard deviations and UMIN (the minimum U value) are printed next. The molar extinction coefficients of all species of interest are written out at each wavelength. The experimental and calculated absorbance readings are printed out for each solution at all wavelengths. The final step in MAIN is to plot the calculated molar extinction coefficients versus wavelength.

EQUIL subroutine calculates the concentrations of all species from initial approximations to the equilibrium constants and an assumed model of the system. Subroutine NEWTRS, used by EQUIL, solves polynomial equations for the unknown concentrations.

ECOEF subroutine calculates the unknown molar extinction coefficients using DETER3 and DETER4 to evaluate third-order and fourth-order determinants. The error-square sum is calculated also.

TWIST subroutine performs the variation of each unknown constant and stores the various U values calculated in ECOEF. The improved SH matrix is calculated in TWIST also. Subroutines MATIN, matrix inversion, PINUS, multiplication of a matrix and a vector, and MULLE, matrix multiplication are used in TWIST and MAIN to perform matrix operations described earlier.

Subroutine PLOT is called by MAIN to plot the molar extinction coefficients. Subroutine POT is used by the PLOT routine.

EQUIL for Ligand Solutions

This subroutine is the same as used by Thomson (68). Stepwise dissociation constants for ligands, H_3L, with three replaceable protons are converted to the corresponding formation constants, K_i, i = 1, 2, and 3. The fraction, α_0, of the total ligand as the unprotonated species, L, is defined in Equation (60), where [H] is the hydrogen-ion concentration.

$$\alpha_0 = 1/(1 + K_1[H] + K_1K_2[H]^2 + K_1K_2K_3[H]^3) \qquad (60)$$

Equilibrium concentrations of all species are then calculated using the equations given in Equation (61) where C_L is the total ligand concentration.

$$\begin{aligned} [L] &= C_L\alpha_0 \\ [HL] &= C_L\alpha_0K_1[H] \\ [H_2L] &= C_L\alpha_0K_1K_2[H]^2 \\ [H_3L] &= C_L\alpha_0K_1K_2K_3[H]^3 \end{aligned} \qquad (61)$$

EQUIL for Metal-Ligand Solutions

A number of different models of species in solution were used in an attempt to fit the data of solutions of Sn(IV) and Pyrocatechol Violet. All were a simple variation of the following model which gave the best fit.

In this model, it is assumed that three complexes, $Sn(H_2PV)^{2+}$, $Sn(H_2PV)_2$, and $Sn_2(H_2PV)^{6+}$, form. The over-all formation constants are defined as shown in Equations (62), (63), and (64). Charges are omitted.

$$[Sn][H_3PV]\beta_{11} = [Sn(H_2PV)][H] \tag{62}$$

$$[Sn][H_3PV]^2\beta_{12} = [Sn(H_2PV)_2][H]^2 \tag{63}$$

$$[Sn]^2[H_3PV]\beta_{21} = [Sn_2(H_2PV)][H] \tag{64}$$

The mass balance for the ligand and metal are given in Equations (65) and (66).

$$C_{PCV} = [H_3PV] + [Sn(H_2PV)] + 2[Sn(H_2PV)_2] + [Sn_2(H_2PV)] \tag{65}$$

$$C_{Sn} = [Sn] + [Sn(H_2PV)] + [Sn(H_2PV)_2] + 2[Sn_2(H_2PV)] \tag{66}$$

Substituting in Equations (65) and (66) for $[Sn(H_2PV)]$, $[Sn(H_2PV)_2]$, and $[Sn_2(H_2PV)]$ from Equations (62), (63), and (64), two equations in two unknowns, $[H_3PV]$ and $[Sn]$, are obtained.

$$[H_3PV] + \beta_{11}[Sn][H_3PV]/[H] + 2\beta_{12}[Sn][H_3PV]^2/[H]^2$$

$$+ \beta_{21}[Sn]^2[H_3PV]/[H] - C_{H_3PV} = 0 \tag{67}$$

$$[Sn] + \beta_{11}[Sn][H_3PV]/[H] + \beta_{12}[Sn][H_3PV]^2/[H]^2 + 2\beta_{21}[Sn]^2[H_3PV]/[H] - C_{Sn} = 0 \qquad (68)$$

These two equations are solved in subroutine EQUIL. Initial approximations, $[H_3PV] = C_{PCV}$ and $[Sn] = C_{Sn}$, are made and Equation (67) is solved for $[H_3PV]$ by Newton's method using NEWTRS. The calculated root is checked to make sure that:

(a) it is not negative

(b) it is less than C_{PCV}

(c) convergence has occurred.

If this root is adequate, it is used to solve Equation (68) for [Sn] by Newton's method. If the new root for [Sn] is adequate, it is compared to the old approximation to the root, and if these agree to three decimal places, it is considered that [Sn] and $[H_3PV]$ have been approximated with sufficient accuracy. If roots are approximated that do not fulfill any of the above criteria, the calculation is terminated.

From Equations (62), (63), and (64) the concentrations of $Sn(H_2PV)^{2+}$, $Sn(H_2PV)_2$, and $Sn_2(H_2PV)^{6+}$ are calculated using the two roots. These concentrations are then returned to ECOEF for use in the calculation of molar extinction coefficients.

CHAPTER VII

EXPERIMENTAL

Reagents

H_2O

Distilled H_2O which had been passed through a mixed cation-anion exchange resin was used throughout this work. Fisher Certified Rexyn 300 resin of medium porosity in H^+ and OH^- ion form was used. The specific conductance of the H_2O after passing through the resin was 6.4×10^{-7} $ohm^{-1} cm^{-1}$. All references will refer to this as distilled H_2O.

Pyrocatechol Violet

The pyrocatechol violet (PCV or 3,3',4'-trihydroxyfuchsone-2"-sulfonic acid) used was Eastman reagent grade. Stock solutions of PCV were prepared by dissolving appropriate amounts of the reagent in distilled water and diluting to volume. These solutions were found to be stable for at least 30 days. In this work fresh solutions were prepared weekly to avoid possible air oxidation of the PCV.

Tin

Baker Analyzed Reagent grade sodium stannate, $Na_2SnO_3 \cdot 3H_2O$, was heated at 160°C for approximately 24 hours to remove water of hydration.

Stock Sn(IV) solutions were prepared by dissolving Na_2SnO_3 in 6.13 M HCl. Solutions prepared with 1M HCl in excess of the component Sn(IV) have been found to be stable for over two years (69).

Hydrochloric Acid

A stock solution of about 6M HCl was prepared by diluting 37.7% Baker Analyzed Reagent grade HCl with distilled H_2O. This solution was then standardized using primary standard Na_2CO_3. All stock Sn(IV) solutions were prepared using this standard acid.

Sodium Chloride

A stock solution of 3M NaCl was prepared by dissolving Baker Analyzed Reagent grade NaCl in distilled H_2O. This solution was used to provide a constant ionic medium of 1M Cl^- for all measurements.

Apparatus

Glassware

All glassware used was Pyrex and volumetric glassware met ACS requirements. Only Class A volumetric glassware was used.

Cells

Scientific Cell Company fused silica cells were used. The matched cells were rectangular with a one centimeter path length. These cells were cleaned with concentrated HNO_3 after use and were stored in a dilute HNO_3 solution between runs.

Instruments

Balance

All weighings were performed on a Mettler Type H5 balance. Samples were weighed to ± 0.0001 grams.

pH Meter

A Beckman Zeromatic pH meter equipped with a Sargent/Jena S-30080-15C saturated calomel reference electrode and a Sargent/Jena S-30050-15C glass electrode was used for all pH measurements. The pH meter was standardized before use with buffers prepared from pHydrion Buffer powders.

Spectrophotometers

Preliminary absorbance measurements were made with a Beckman Model DU Quartz Spectrophotometer. All later work was done on a dual beam Cary Recording Spectrophotometer, Model 14. All studies were in the visible or ultraviolet regions of the spectrum. Unless stated otherwise, spectra were recorded from 7000 Å to 2400 Å at a rate of 5 Å/sec and a chart speed of 2 in/min. This gave a wavelength scale of 50 Å/ scale division. The readings of the baseline and cells were checked regularly. Absorbance readings were taken from the spectra of the solutions at 50 Å (5mμ) intervals. All readings were estimated to ± 0.001 absorbance units. These absorbance readings were then punched onto computer cards for analysis.

Solutions

Pyrocatechol Violet

Pyrocatechol violet (PCV) is a reddish-brown crystalline powder which is readily soluble in H_2O. The spectra of several solutions of varying concentrations of PCV in distilled H_2O were determined to find a suitable concentration range for spectrophotometric studies. Stock solutions of PCV were prepared by dissolving 0.1932 grams of reagent grade PCV in distilled H_2O and diluting to 500 ml. The pH's of these 10^{-3} M PCV solutions were approximately 4.5.

A series of 10^{-4} M PCV solutions were prepared, over a period of one week, by diluting 10 ml of the stock solution to 100 ml. The absorbances of each of these solutions were measured at several wavelengths between 5000 Å and 2500 Å. No changes were observed over a period of one week. Therefore, fresh PCV stock solutions were prepared weekly.

Since PCV shows acid-base indicator properties with color transitions in both acidic and alkaline pH ranges, it was necessary to study the spectrum of PCV as a function of pH. PCV is apparently present in several forms in the pH range from 0 to 7 due to the ionization of the sulfonic acid group and then the loss of hydroxyl protons as the pH is increased (57). The PCV concentration used was 8×10^{-5} M in 1M Cl^-. The spectra of 9 solutions were obtained. The pH was adjusted with HCl or NaOH solutions. The wavelength range was 7000 Å to 2600 Å. The reference solution was 1M Cl^-. The solution compositions are given in Table III.

TABLE III

PCV AS f(pH)

Solution Number	PCV	Volume 10^{-3}M PCV (ml)	pH	Volume 2M HCl (ml)	Volume 3M NaCl (ml)
1	8×10^{-5}M	4.0	0.42	22.00	2.00
2	8×10^{-5}M	4.0	1.01	2.50	15.00
3	8×10^{-5}M	4.0	2.02	0.25	16.50
4	8×10^{-5}M	4.0	3.05	0.00	16.66
5	8×10^{-5}M	4.0	4.09	0.00	16.66
6	8×10^{-5}M	4.0	5.20	0.00	16.66
7	8×10^{-5}M	4.0	6.03	0.00	16.66
8	8×10^{-5}M	4.0	7.11	0.00	16.66
9	8×10^{-5}M	4.0	8.18	0.00	16.66

The spectra of another series of PCV solutions were determined with the PCV concentrations ranging from 2×10^{-5} M to 7×10^{-5} M in 1M Cl^-. The pH of each solution was adjusted to 3.00 ± 0.05 with HCl or NaOH. The reference solution was 1M NaCl. The wavelength range was 7000 Å to 2600 Å. The compositions of these solutions are given in Table IV.

TABLE IV

COMPOSITION OF PCV SOLUTIONS AT pH 3.00

Solution Number	Volume 10^{-3} M PCV (ml)	C_{PCV}	Volume 3 M NaCl (ml)
1	1.0	2×10^{-5} M	16.66
2	1.5	3×10^{-5} M	16.66
3	2.0	4×10^{-5} M	16.66
4	2.5	5×10^{-5} M	16.66
5	3.0	6×10^{-5} M	16.66
6	3.5	7×10^{-5} M	16.66

Stock Sn(IV) Solutions

The procedure for the preparation of stock Sn(IV) solutions was to dry reagent grade sodium stannate, $Na_2SnO_3 \cdot 3H_2O$, at 160°C for 24 hours to assure loss of water of hydration. Then the required amounts of Na_2SnO_3 needed to yield stock solutions of the concentrations shown in Table V were weighed out and dissolved in 6.13 M HCl.

TABLE V

COMPOSITION OF STOCK Sn(IV) SOLUTIONS

Series Number	Grams Na_2SnO_3/ 500 ml HCl	C_{Sn}
I	0.5318	5.0×10^{-3} M
II	1.0636	1.0×10^{-2} M
III	1.5955	1.5×10^{-2} M
IV	2.1273	2.0×10^{-2} M

Tin-Pyrocatechol Violet Solutions

Preliminary runs on PCV solutions, Sn(IV) solutions, and mixtures of PCV and Sn(IV) indicated no absorption bands in the wavelength range from 18,000 Å to 7000 Å. Therefore, all measurements were restricted to the range 7000 Å to 2400 Å. The visible and ultraviolet spectrum of each solution in each series of solutions was obtained. Four series of solutions, each with a different total Sn(IV) concentration, were studied. The compositions of these solutions are given in Tables VI, VII, VIII, and IX.

The following procedure was used to prepare the solutions given in Tables VI, VII, VIII, and IX. A 10 ml aliquot of a particular Sn(IV) stock solution in 6.13 M HCl was diluted to 100 ml with distilled H_2O. This produces a solution 0.613 M in HCl. This solution is used immediately after dilution. A 1 ml aliquot of a diluted stock Sn(IV) solution is transferred to a 50 ml volumetric flask. The required volume of PCV solution was added and the solution mixed thoroughly.

TABLE VI

Sn-PCV SERIES I

Solution Number	Volume 5×10^{-4} M Sn (IV) in 0.613M HCl (ml)	C_{Sn}	Volume 10^{-3} M PCV (ml)	C_{PCV}	Volume 3.0 M NaCl (ml)	$C_{PCV}:C_{Sn}$
0	1.0	1.0×10^{-5} M	0.25	0.5×10^{-5} M	16.46	1:2
1	1.0	1.0×10^{-5} M	0.5	1.0×10^{-5} M	16.46	1:1
2	1.0	1.0×10^{-5} M	1.0	2.0×10^{-5} M	16.46	2:1
3	1.0	1.0×10^{-5} M	1.5	3.0×10^{-5} M	16.46	3:1
4	1.0	1.0×10^{-5} M	2.0	4.0×10^{-5} M	16.46	4:1
5	1.0	1.0×10^{-5} M	2.5	5.0×10^{-5} M	16.46	5:1
6	1.0	1.0×10^{-5} M	3.0	6.0×10^{-5} M	16.46	6:1
7	1.0	1.0×10^{-5} M	3.5	7.0×10^{-5} M	16.46	7:1

TABLE VII

Sn-PCV SERIES II

Solution Number	Volume 10^{-3} M Sn (IV) in 0.613M HCl (ml)	C_{Sn}	Volume 10^{-3} M PCV (ml)	C_{PCV}	Volume 3.0 M NaCl (ml)	C_{PCV}:C_{Sn}
0	1.0	2.0×10^{-5} M	0.25	0.5×10^{-5} M	16.46	1:4
1	1.0	2.0×10^{-5} M	0.5	1.0×10^{-5} M	16.46	1:2
2	1.0	2.0×10^{-5} M	1.0	2.0×10^{-5} M	16.46	1:1
3	1.0	2.0×10^{-5} M	1.5	3.0×10^{-5} M	16.46	3:2
4	1.0	2.0×10^{-5} M	2.0	4.0×10^{-5} M	16.46	2:1
5	1.0	2.0×10^{-5} M	2.5	5.0×10^{-5} M	16.46	5:2
6	1.0	2.0×10^{-5} M	3.0	6.0×10^{-5} M	16.46	3:1
7	1.0	2.0×10^{-5} M	3.5	7.0×10^{-5} M	16.46	7:2

TABLE VIII

Sn-PCV SERIES III

Solution Number	Volume 1.5×10^{-4} M Sn (IV) in 0.613M HCl (ml)	C_{Sn}	Volume 10^{-3} M PCV (ml)	C_{PCV}	Volume 3.0 M NaCl (ml)	$C_{PCV}:C_{Sn}$
1	1.0	3.0×10^{-5} M	0.30	0.6×10^{-5} M	16.46	1:5
2	1.0	3.0×10^{-5} M	0.5	1.0×10^{-5} M	16:46	1:3
3	1.0	3.0×10^{-5} M	1.0	2.0×10^{-5} M	16.46	2:3
4	1.0	3.0×10^{-5} M	1.5	3.0×10^{-5} M	16.46	1:1
5	1.0	3.0×10^{-5} M	2.0	4.0×10^{-5} M	16.46	4:3
6	1.0	3.0×10^{-5} M	2.5	5.0×10^{-5} M	16.46	5:3
7	1.0	3.0×10^{-5} M	3.0	6.0×10^{-5} M	16.46	2:1

TABLE IX

Sn-PCV SERIES IV

Solution Number	Volume 2.0×10^{-3} M Sn (IV) in 0.613M HCl (ml)	C_{Sn}	Volume 10^{-3} M PCV (ml)	C_{PCV}	Volume 3.0 M NaCl (ml)	$C_{PCV}:C_{Sn}$
1	1.0	4.0×10^{-5} M	0.33	0.66×10^{-5} M	16.46	1:6
2	1.0	4.0×10^{-5} M	0.5	1.0×10^{-5} M	16.46	1:4
3	1.0	4.0×10^{-5} M	1.0	2.0×10^{-5} M	16.46	1:2
4	1.0	4.0×10^{-5} M	1.25	2.5×10^{-5} M	16.46	5:8
5	1.0	4.0×10^{-5} M	1.5	3.0×10^{-5} M	16.46	3:4
6	1.0	4.0×10^{-5} M	2.0	4.0×10^{-5} M	16.46	1:1
7	1.0	4.0×10^{-5} M	2.5	5.0×10^{-5} M	16.46	5:4

Color development was immediate upon mixing. After adding 16.46 ml of 3.0 M NaCl, the solution was diluted to 50 ml with distilled H_2O. This produces 50 ml of solution containing approximately 0.6 milliequivalents H^+. A constant ionic strength of 1M Cl^- was used in all measurements. The flask was shaken to assure complete mixing. The contents were then transferred to a 150 ml beaker and the pH adjusted to 3.00 ± 0.05 with 1M NaOH. The maximum amount of 1M NaOH required was 0.6 ml so the dilution error was negligible. After adjusting the pH, the spectrum was obtained using a reference solution of 1M NaCl in H_2O. The spectrum was obtained from 7000 Å to 2400 Å using a Cary 14 recording spectrophotometer.

CHAPTER VIII

RESULTS AND DISCUSSION

Pyrocatechol Violet

Ross and White (2) state that pyrocatechol violet forms at least two complexes with tin(IV). Their results indicate that the optimum pH for the formation of these complexes is between 2.5 and 3.0. For this reason all tin(IV)-pyrocatechol violet solutions were studied at pH 3.00. However, since pyrocatechol violet shows color transitions in both acidic and basic media (57), it was necessary to study the pyrocatechol violet system both as a function of pH and at pH 3.00 before trying to interpret the tin(IV)-pyrocatechol violet system. The stepwise equilibria used to interpret the pyrocatechol violet data were first proposed by Suk and Malat (57).

The undissociated molecule shown earlier will be represented as H_4PV. The proposed equilibria are given in Equations (69), (70), and (71) with the stepwise dissociation constants given in Equations (72), (73), and (74).

$$H_4PV \underset{}{\overset{k_1}{\rightleftharpoons}} H_3PV^- + H^+ \tag{69}$$

$$H_3PV^- \underset{}{\overset{k_2}{\rightleftharpoons}} H_2PV^{2-} + H^+ \tag{70}$$

$$H_2PV^{2-} \underset{}{\overset{k_3}{\rightleftharpoons}} HPV^{3-} + H^+ \tag{71}$$

$$k_1 = [H_3PV^-][H^+]/[H_4PV] \quad (72)$$

$$k_2 = [H_2PV^{2-}][H^+]/[H_3PV^-] \quad (73)$$

$$k_3 = [HPV^{3-}][H^+]/[H_2PV^{2-}] \quad (74)$$

The spectra of the series of solutions given in Table III were obtained to determine the number of absorbing species in solution as a function of pH and to determine the acid dissociation constants of pyrocatechol violet. The spectra obtained are given in Figures 5 and 6. Color transitions occur in the pH ranges 1-2 and 5-6. The solutions are red in strongly acid media, yellow from pH 2 to 5, and violet above pH 6. No other color changes occur as the pH is increased to 8.18. Higher pH's were not used because of the apparent decomposition of pyrocatechol violet in strongly basic solutions. Solutions of pH 9 and 10 were violet but upon acidification, the observed absorbances at 440 and 550 mμ were greatly reduced. It has been reported that air oxidation of pyrocatechol violet occurs in basic solutions (57).

Number of Absorbing Species

The absorbance data from the spectra in Figures 5 and 6 were used as input data for the matrix rank calculation. Several combinations of solutions were used. Absorbance readings from 700 to 260 mμ at 5 mμ intervals were used in each case. The absorbance and error matrices were 89 x 9 for solutions 1 through 9, 89 x 5 for solutions 1 through 5, and 89 x 7 for solutions 3 through 9. The error matrix was calculated using Equation (13) with the accepted value being that for which the photometric error, ΔT, was 0.005. Too small a photometric error will

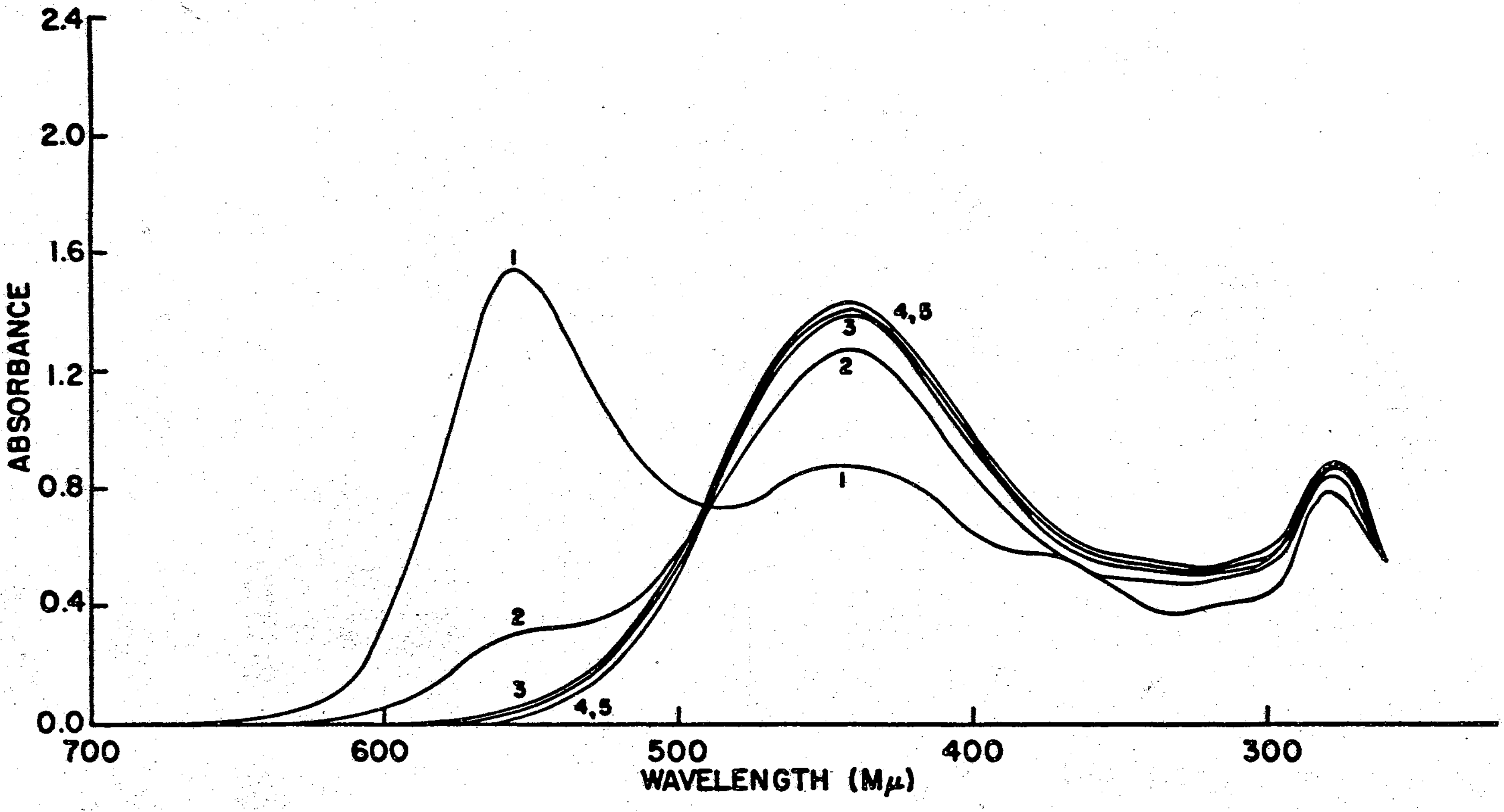


Figure 5. Pyrocatechol Violet as f(pH)-Solutions 1,2,3,4,5

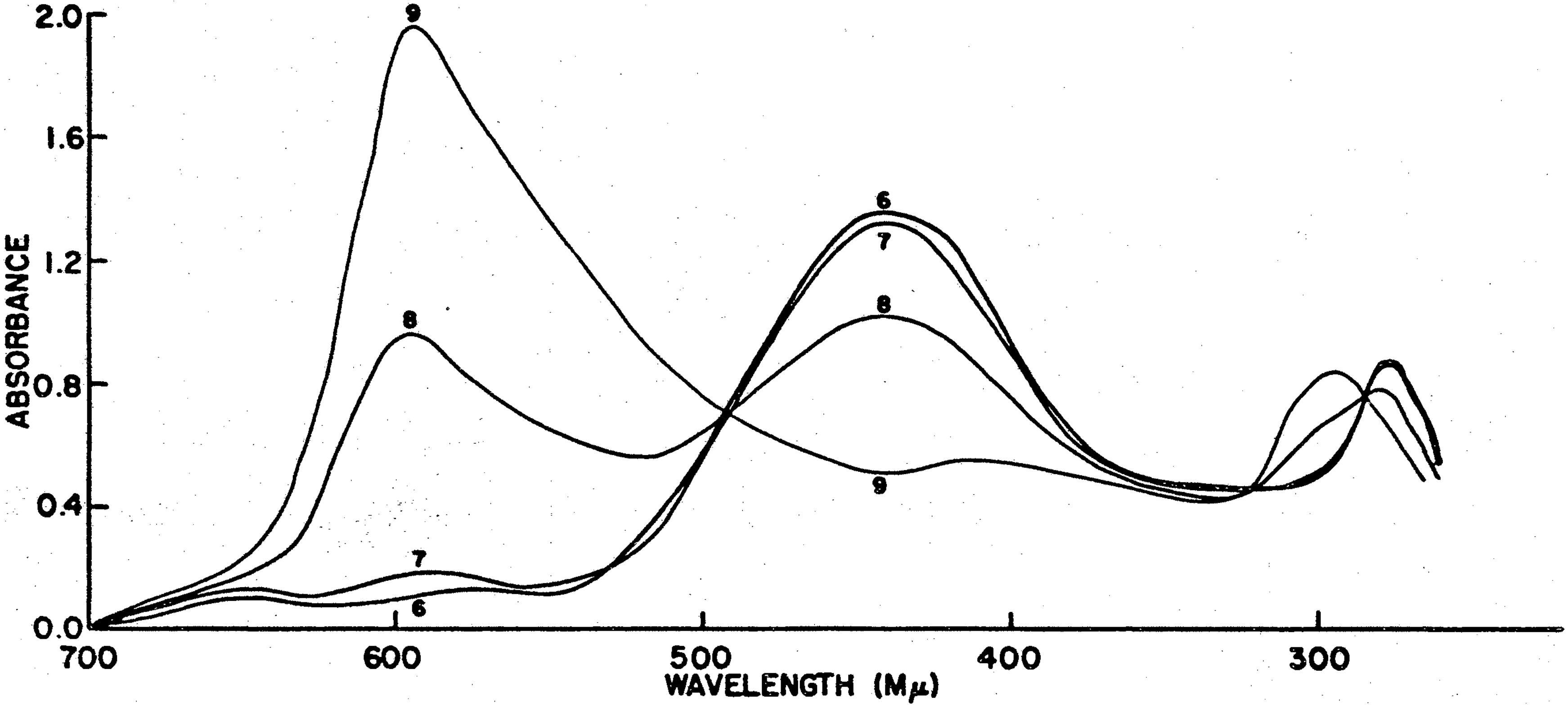


Figure 6. Pyrocatechol Violet as f(pH)-Solutions 6,7,8,9

cause noise on the absorbance surface to be counted as an absorbing species. Too large a value, on the other hand, will treat a significant absorbing species as noise. The results of the rank calculations are summarized in Table X.

TABLE X

NUMBER OF ABSORBING SPECIES IN PYROCATECHOL VIOLET SOLUTIONS OF VARYING pH

ΔT	Rank Solutions 1-9	 Solutions 1-5	 Solutions 3-9
0.001	6	3	5
0.002	5	3	4
0.003	4	2	3
0.004	4	2	3
0.005	4*	2*	3*
0.006	4	2	3
0.007	4	2	3
0.008	4	2	3
0.009	4	2	3
0.010	4	2	3

*Accepted value.

Matrix rank analysis indicated the presence of four absorbing species over the entire pH range with two species in the first five solutions. The species which absorbs strongly at 550 mμ in solutions

1 and 2 is the undissociated molecule, H_4PV. Then, between pH 1 and 2, this peak diminishes quickly as the solution color changes from red to yellow. This is due to the ionization of the sulfonic acid group. The reaction occurring is given in Equation (69). It is evident from the spectra that the singly charged anion, H_3PV^-, exists as the predominant species over the pH range from 2 to 5. The maximum absorbance of this species occurs at 440 mμ. Between pH 5 and 6, another color change occurs. This color change is due to the reactions given in Equations (70) and (71).

The rank of four observed for solutions 1 through 9 is due to the presence of the four species given in the equilibria described in Equations (69), (70), and (71). The rank of two observed for solutions 1 through 5 is due to the equilibrium given in Equation (69) and the rank of three for solutions 3 through 9 is due to the presence of the three species described in Equations (70) and (71).

Acid Dissociation Constants of Pyrocatechol Violet

The acid dissociation constants of pyrocatechol violet were determined from the spectra of the solutions listed in Table III. The calculations were done with the pit-mapping program using the EQUIL subroutine described earlier. The concentrations of each form of pyrocatechol violet in each solution and the molar extinction coefficients of each species at all wavelengths were also calculated.

The spectra of the solutions between 620 and 260 mμ and their acidities were used as the primary input data. The concentration of pyrocatechol violet, 8.0×10^{-5} M, was entered and the initial estimates, 0.260, 7.200, and 8.000 of pK_1, pK_2, and pK_3, respectively, were used.

The estimates of 7.200 and 8.000 for pK_2 and pK_3 were obtained from Ryba and coworkers (70). The pK_1 value of 0.260 was of the proper order of magnitude for a sulfonic acid (71). These estimates were varied by the procedure described earlier with the initial value of DEC = 0.10. The pit-mapping calculation was performed on solutions 1 through 9, 1 through 5, and 3 through 9. The models used in EQUIL for each case were derived from the equilibria given in Equations (69), (70), and (71).

The successful model for solutions 1 through 9 is summarized in Equations (69), (70), and (71). The initial estimates for pK_1, pK_2, and pK_3 were 0.260, 7.200, and 8.000, respectively. Six iterations were required for convergence with the following results obtained:

$$pK_1 = 0.264 \pm 0.003$$

$$pK_2 = 7.508 \pm 0.001$$

$$pK_3 = 8.332 \pm 0.003$$

UMIN, the minimum error-square sum, was 0.982. The typical size of UMIN for a good fit is from 10^{-2} to 10^{1}. The molar extinction coefficients of four pyrocatechol violet species were calculated; these are plotted in Figures 7 and 8 and are given in Table XIX. The concentrations of each species in each solution were calculated and plotted in Figure 9 as a function of pH.

As expected, no convergence was obtained for any two or three species model tried on solutions 1 through 9. The evidence for lack of convergence is: large values (10^{10} - 10^{15}) for the error-square sum, large standard deviations for the equilibrium constants, negative molar

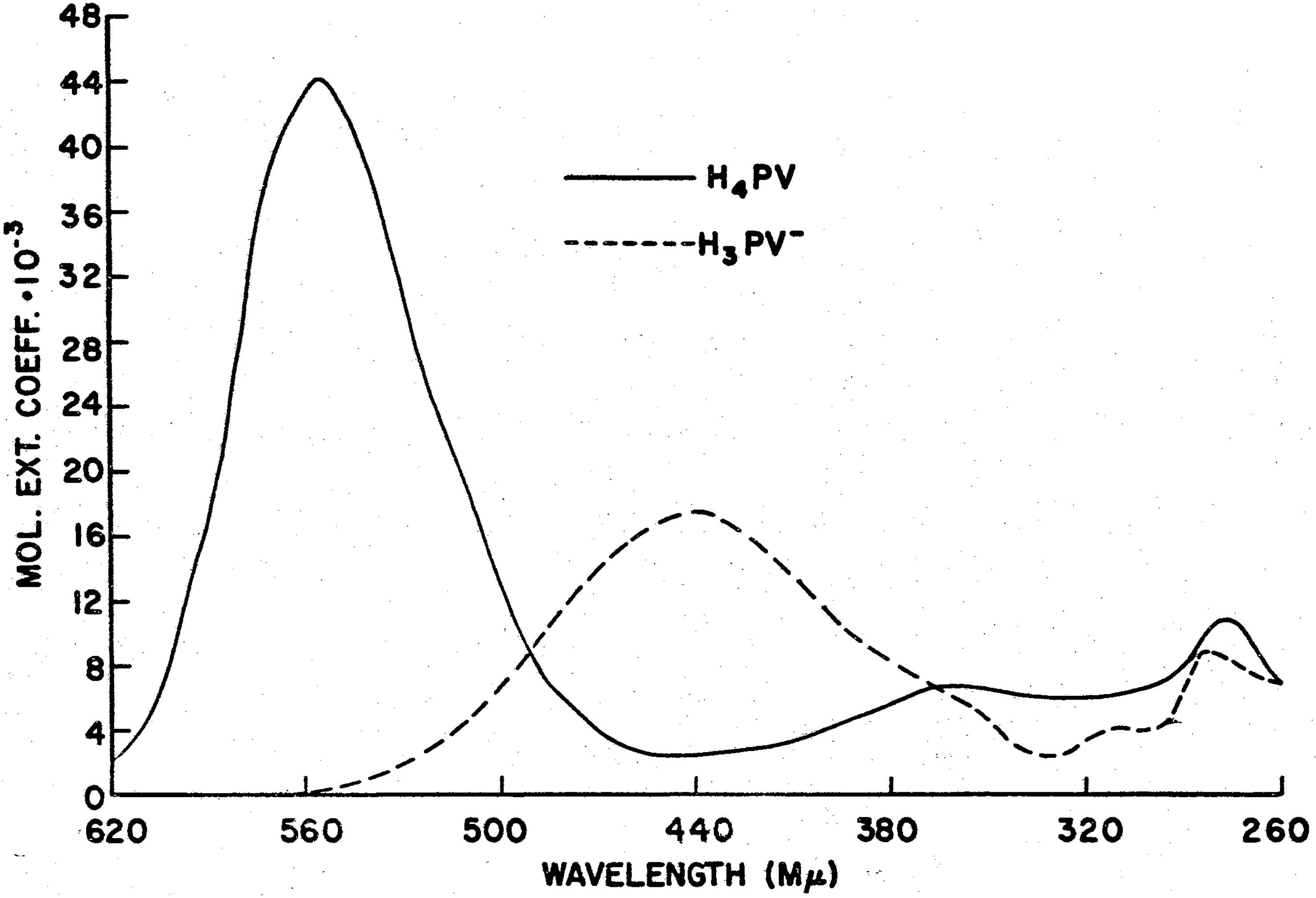


Figure 7. Molar Extinction Coefficients of H_4PV and H_3PV^-

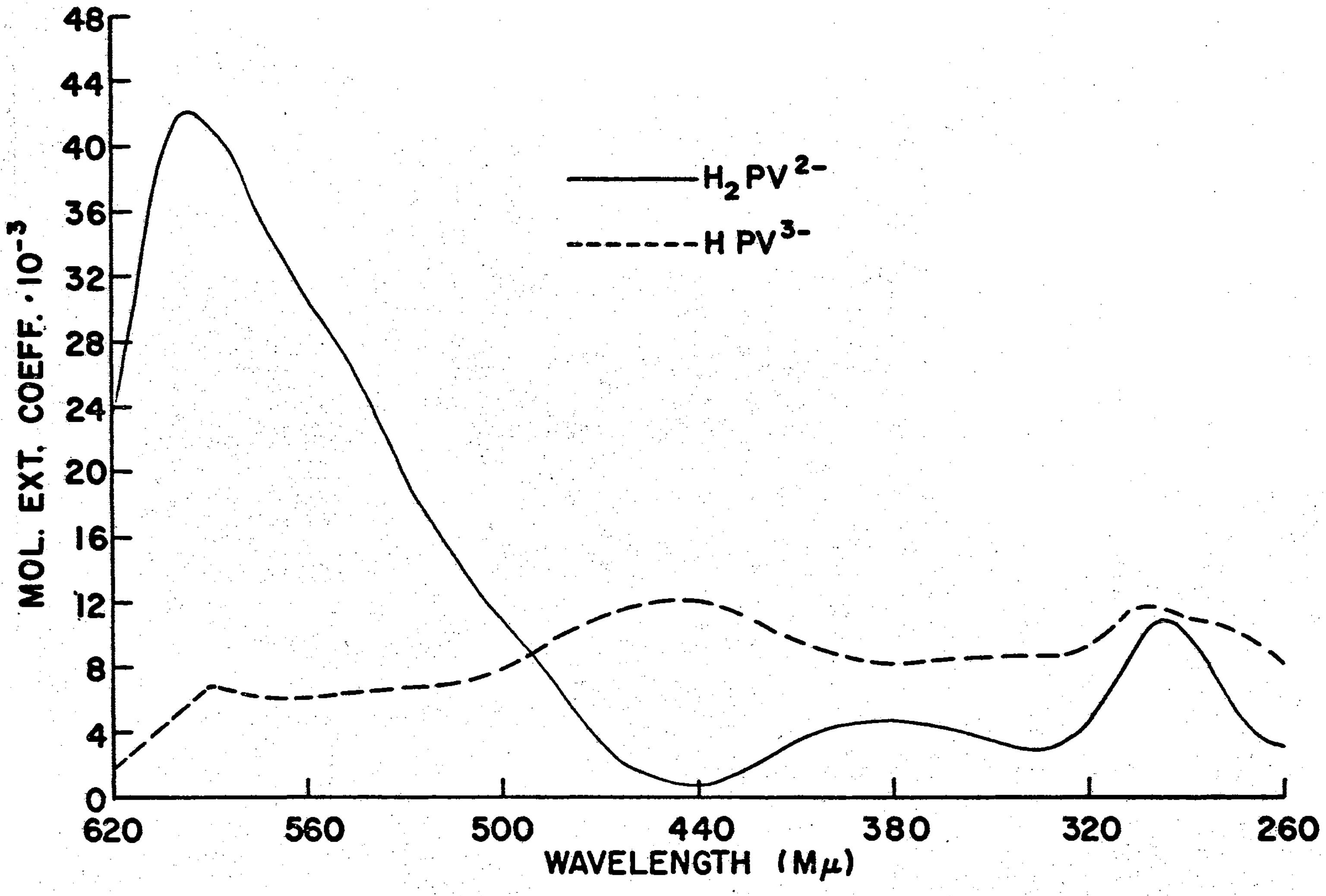


Figure 8. Molar Extinction Coefficients of H_2PV^{2-} and HPV^{3-}

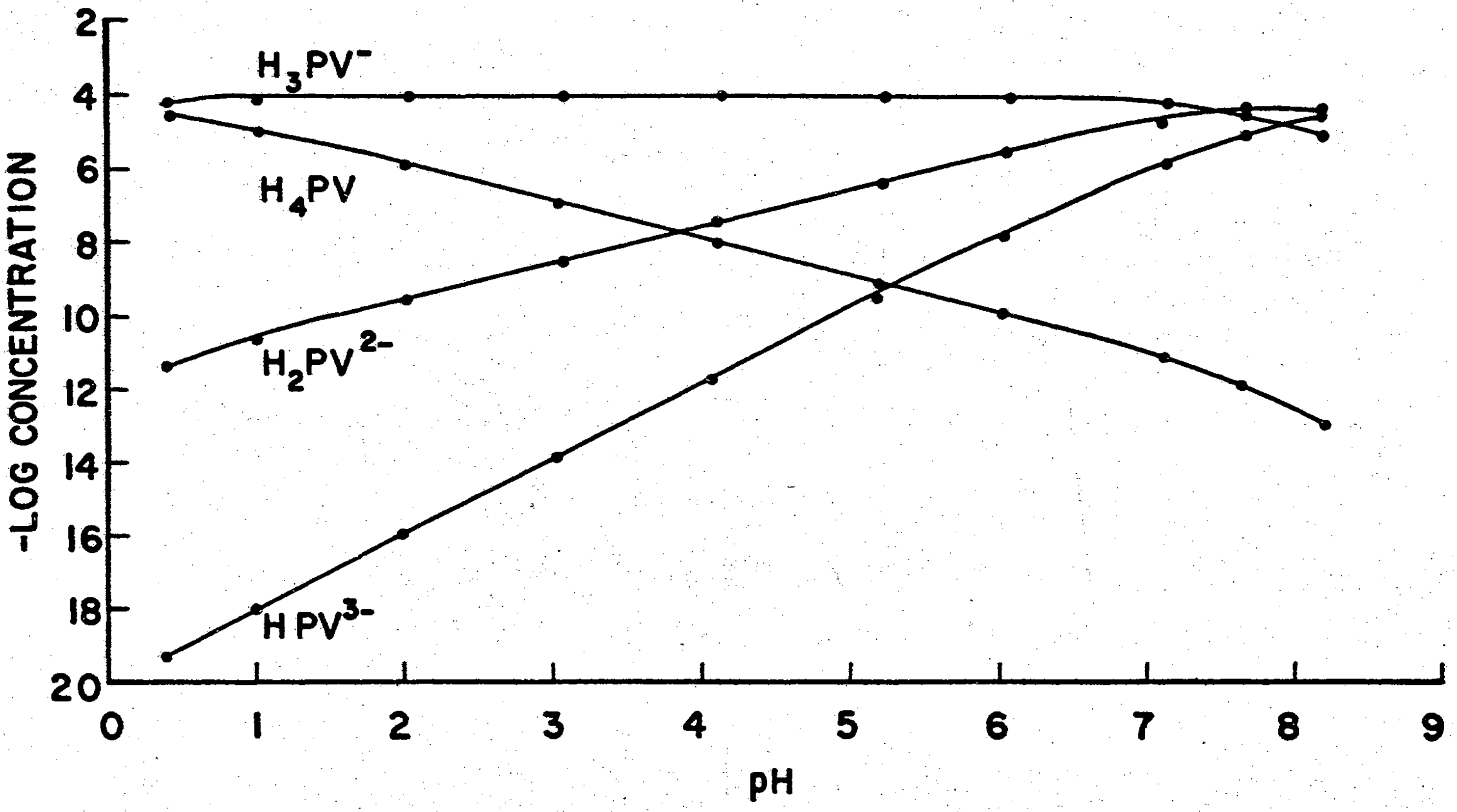


Figure 9. Concentrations of Pyrocatechol Violet Species

extinction coefficients, exceptionally large molar extinction coefficients, a zero value for the concentration determinant in ECOEF, or inadequate roots in EQUIL.

Pit-mapping calculations were also performed on solutions 1 through 5. The input value for pK_1 was 1.00 with the initial value of DEC = 0.10. The model for the system is given by Equation (69). The value for pK_1 obtained was 0.262 ± 0.004 which is in excellent agreement with the earlier value for pK_1. UMIN was 0.582.

The input estimates for pK_2 and pK_3 for the calculation on solutions 3 through 9 were 7.360 and 8.120, respectively. The initial value for DEC was 0.10. The model used in subroutine EQUIL is given in Equations (70) and (71). The calculated values for pK_2 and pK_3 are

$$pK_2 = 7.223 \pm 0.024$$

$$pK_3 = 8.038 \pm 0.031 \quad .$$

The minimum error-square sum was 0.197. The pK's are in good agreement with the four species model calculation on solutions 1 through 9.

Concentrations and molar extinction coefficients calculated in the last two cases agreed quite well with the values obtained from the four species model. However, since the four species model treats all of the data simultaneously, the results obtained in that case are assumed to be the best values. The results given in Figures 7, 8, and 9, and Table XIX were from the four species calculation.

The values obtained for pK_2 and pK_3 are in good agreement with those calculated by Ryba (70). No literature value for pK_1 was found.

Pyrocatechol Violet at pH 3.00

The spectra of the pyrocatechol violet solutions given in Table IV are shown in Figure 10. The purpose of this series of solutions was to determine the number of species in solution at pH 3.00. From the equilibria and spectra described earlier, it was suspected that only one species was present in significant amounts. The concentration diagram of Figure 9 shows that H_3PV^-, the singly charged anion due to ionization of the sulfonic acid group, is the predominant species at pH 3.00.

The results of the matrix rank calculation on the spectra given in Figure 10 are shown in Table XI. Absorbance readings from 660 to 265 mμ at 5 mμ intervals were used as input data. The absorbance and error matrices were 80 x 6. As expected, there is one absorbing species of pyrocatechol violet present in solution at pH 3.00. The absorbing species is H_3PV^-.

The species number program was run on the above data, with only the one absorbing species case being tried. The results are shown in Figure 11. The X and Y absorbance functions given by Equation (19) in Chapter IV were plotted for six solutions and eight different wavelengths. The best straight line fit was calculated for each line. The result, a series of straight lines through the origin, indicates one absorbing species present in solution. SMIN, the goodness-of-fit parameter, ranged from 0.013 to 1.32. These values indicated correct weighting of the data points, since SMIN based on the Chi-squared distribution should have values on the order of unity.

Beer's law plots were made from the absorbance readings at 440 and 280 mμ. Over the concentration range studied Beer's law is obeyed.

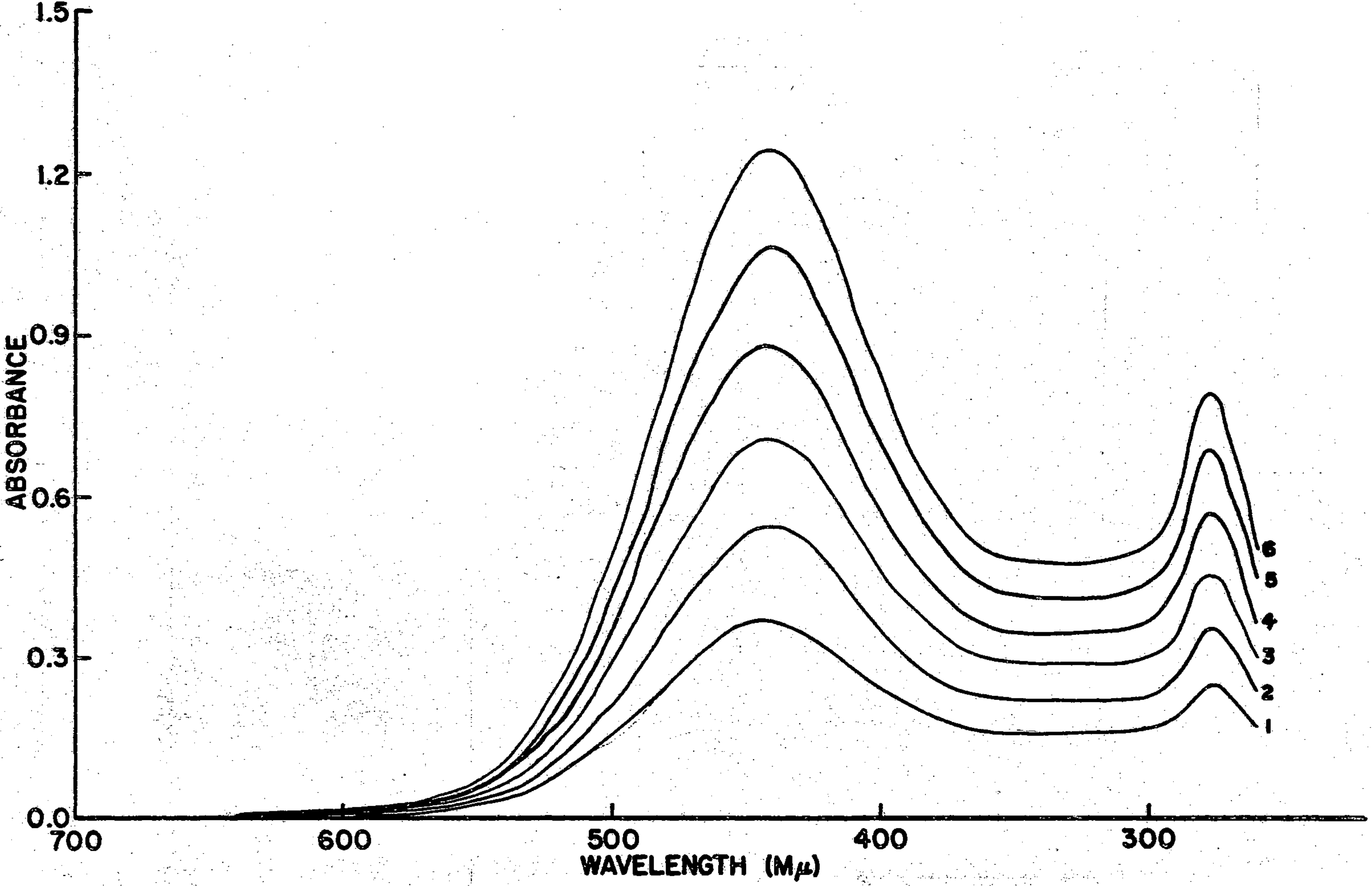


Figure 10. Pyrocatechol Violet at pH 3.00

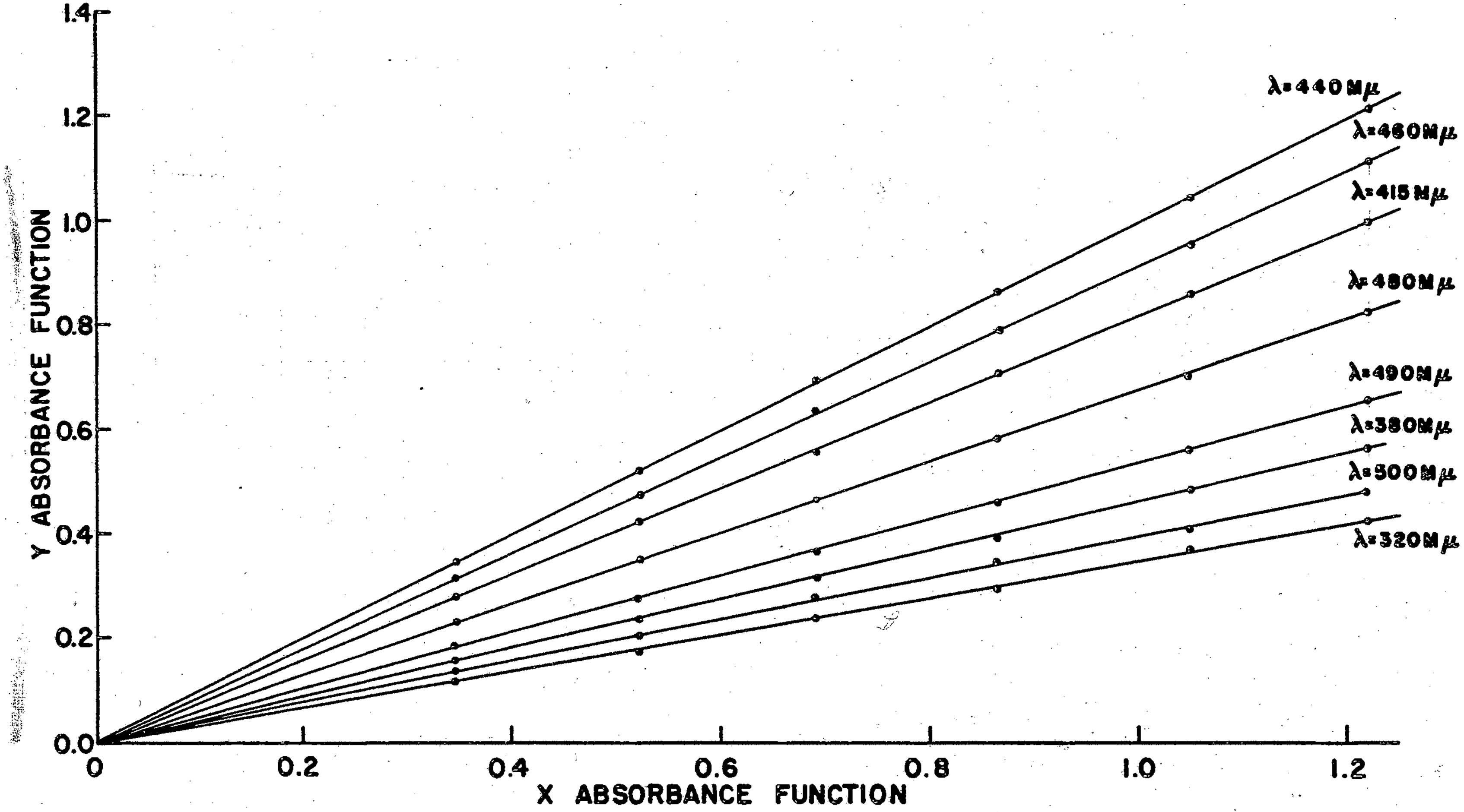


Figure 11. Species Number Plot, PCV at pH 3.00

TABLE XI

NUMBER OF ABSORBING SPECIES IN PYROCATECHOL VIOLET SOLUTIONS AT pH 3.00

ΔT	Rank (Solutions 1-6)
0.001	4
0.002	1
0.003	1
0.004	1
0.005	1*
0.006	1
0.007	1
0.008	1
0.009	1
0.010	1

*Accepted value.

Using Beer's law, the molar extinction coefficients of H_3PV^- were calculated. The agreement between these values and those calculated using the pit-mapping program is excellent. The molar extinction coefficient at 440 mμ was calculated to be 17,385 using Beer's law and 17,490 using the pit-mapping program. At 280 mμ, the Beer's law calculation gave 10,785 while pit-mapping yielded 10,870. The difference is less than 1%.

Tin (IV)--Pyrocatechol Violet

Number of Absorbing Species

The spectra of each series of solutions given in Tables VI, VII, VIII, and IX are shown in Figures 12, 13, 14, and 15, respectively. The wavelength range was 700 to 240 mμ. In order to determine the number of absorbing species in solution, matrix rank calculations were run on several combinations of solutions in each series. The results are summarized in Tables XII, XIII, XIV, and XV.

The absorbance and error matrices for Series I were 80 x 8 for solutions 0 through 7 and 80 x 7 for solutions 1 through 7. Absorbance readings from 660 to 265 mμ at 5 mμ intervals were used as input data. The number of absorbing species in each case of Series I is three using $\Delta T = 0.005$. However, at $\Delta T = 0.004$, the rank of solutions 0 through 7 is four. This is due to the presence of the small absorption band at 610 mμ in the spectrum of solution 0 shown in Figure 12. The peak at 610 mμ occurs only in those solutions where the ratio $C_{PCV}:C_{Sn}$ is less than one. In Series I only the first solution absorbs appreciably at 610 mμ. The rank of solutions 1 through 7 is three. Since

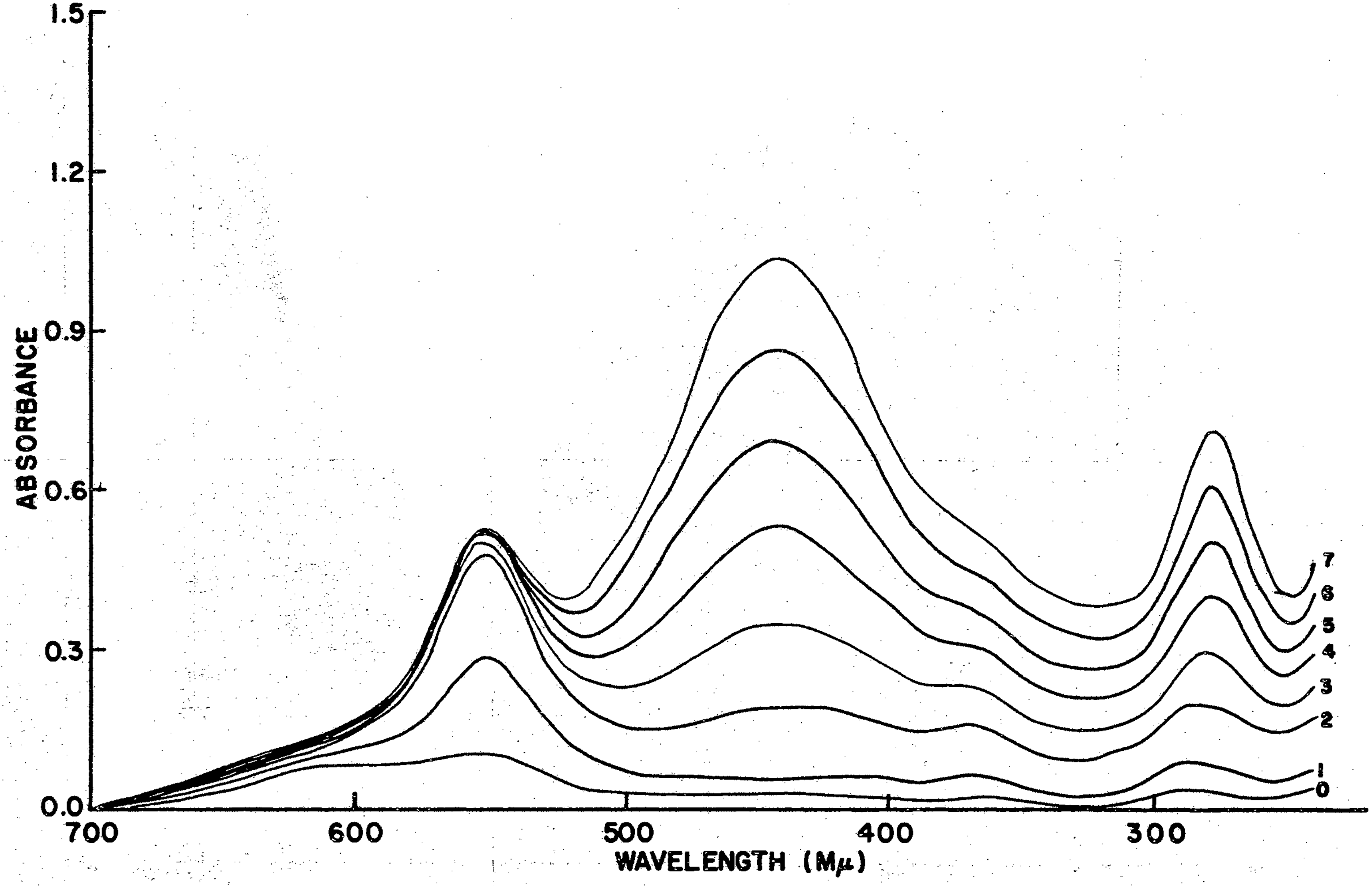


Figure 12. Spectra of Sn-PCV Series I

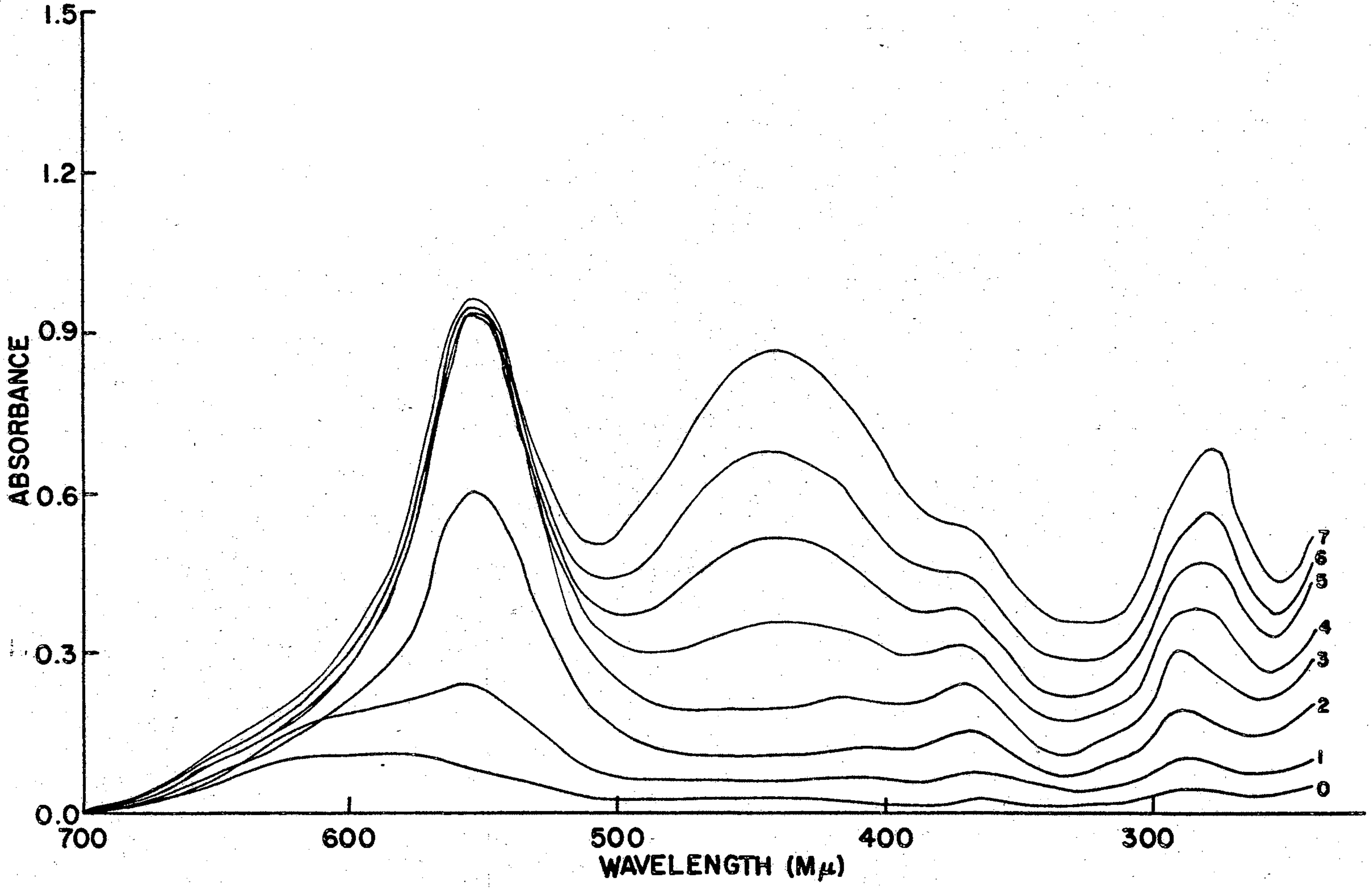


Figure 13. Spectra of Sn-PCV Series II

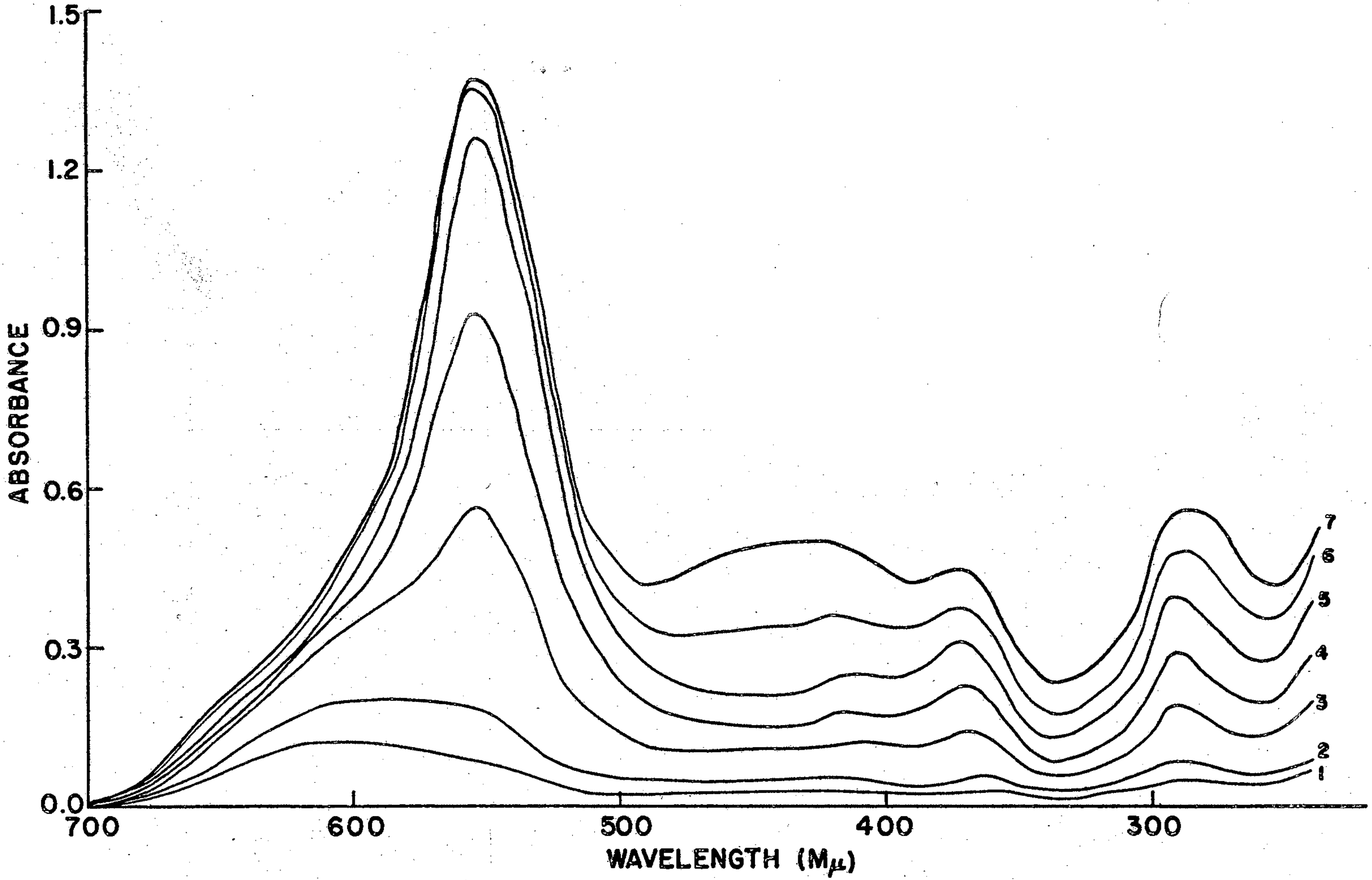


Figure 14. Spectra of Sn-PCV Series III

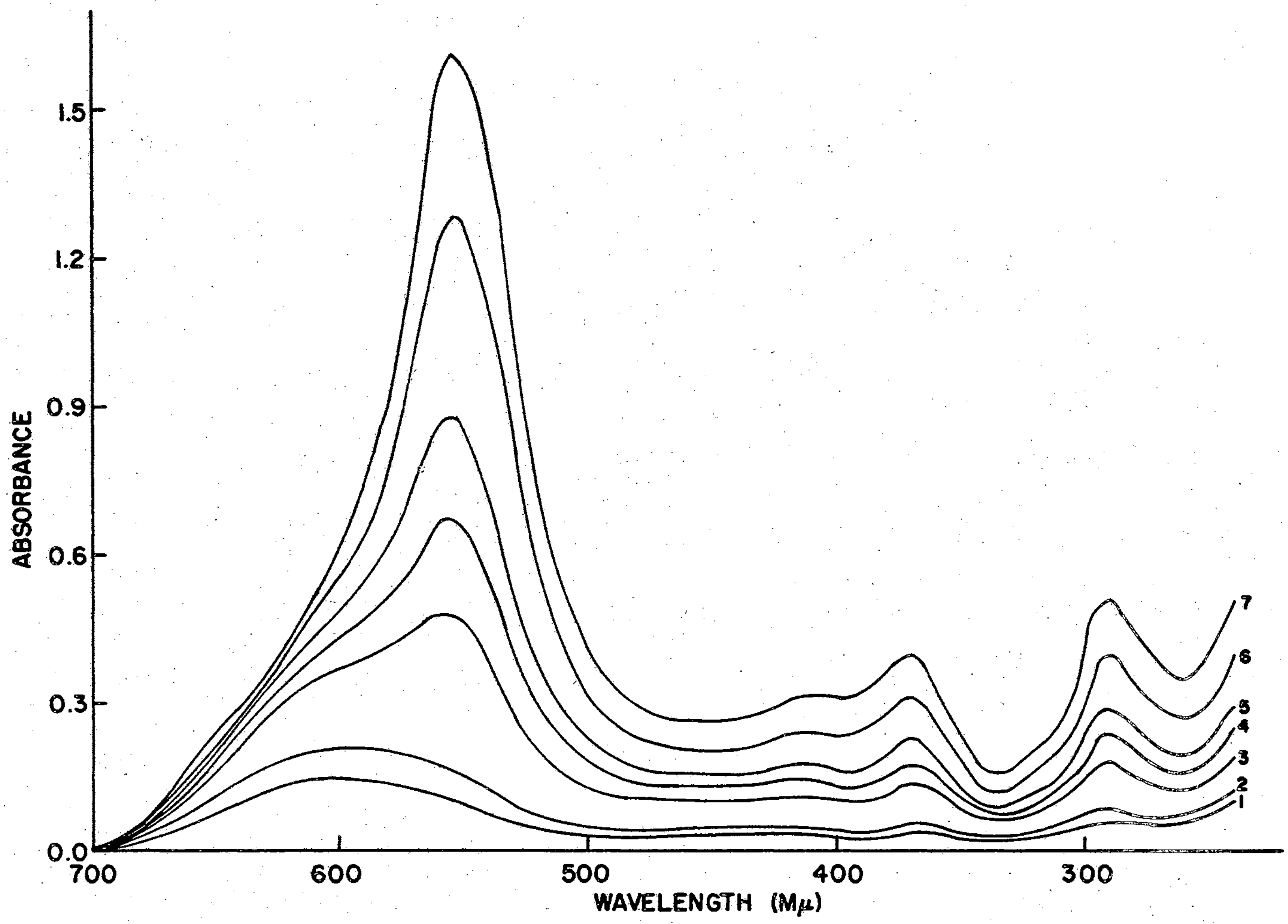


Figure 15. Spectra of Sn-PCV Series IV

TABLE XII

NUMBER OF ABSORBING SPECIES IN SOLUTIONS OF TIN(IV) AND PYROCATECHOL VIOLET-SERIES I

	Rank	
ΔT	Solutions 0-7	Solutions 1-7
0.001	4	3
0.002	4	3
0.003	4	3
0.004	4	3
0.005	3*	3*
0.006	3	3
0.007	3	3
0.008	3	3
0.009	3	3
0.010	3	3

*Accepted value.

TABLE XIII

NUMBER OF ABSORBING SPECIES IN SOLUTIONS OF TIN(IV) AND PYROCATECHOL VIOLET-SERIES II

	Rank	
ΔT	Solutions 0-7	Solutions 2-7
0.001	4	3
0.002	4	3
0.003	4	3
0.004	4	3
0.005	4*	3*
0.006	4	3
0.007	4	2
0.008	4	2
0.009	3	2
0.010	3	2

*Accepted value.

TABLE XIV

NUMBER OF ABSORBING SPECIES IN SOLUTIONS OF TIN(IV) AND PYROCATECHOL VIOLET-SERIES III

	Rank	
ΔT	Solutions 1-7	Solutions 1-5
0.001	4	3
0.002	4	3
0.003	4	3
0.004	4	3
0.005	3*	3*
0.006	3	3
0.007	3	3
0.008	3	2
0.009	3	2
0.010	3	2

*Accepted value.

TABLE XV

NUMBER OF ABSORBING SPECIES IN SOLUTIONS OF TIN(IV) AND PYROCATECHOL VIOLET-SERIES IV

ΔT	Rank(Solutions 1-7)
0.001	3
0.002	3
0.003	3
0.004	3
0.005	3*
0.006	3
0.007	3
0.008	2
0.009	2
0.010	2

*Accepted value.

the free ligand, H_3PV^-, absorbs at 440 mμ and contributes a rank of one, the number of metal-ligand species in Series I is three.

The absorbance and error matrices for Series II were 80 x 8 for solutions 0 through 7 and 80 x 6 for solutions 2 through 7. Absorbance readings from 660 to 265 mμ at 5 mμ intervals were used as input data. The rank of solutions 0 through 7 is four while the rank of solutions 2 through 7 is three. Since H_3PV^- contributes a rank of one to each case, the number of metal-ligand species is three and two for solutions 0 through 7 and 2 through 7, respectively. The difference is due to the absorption band at 610 mμ (Figure 13) which occurs in solutions 0 and 1 where $C_{PCV}:C_{Sn}$ is less than one.

The absorbance and error matrices for Series III were 80 x 7 for solutions 1 through 7 and 80 x 5 for solutions 1 through 5. The wavelength range was from 660 to 265 mμ at 5 mμ intervals. The rank of three for solutions 1 through 5 is due to the presence of three metal-ligand species, since the free ligand absorbance at 440 mμ is negligible. Using $\Delta T = 0.005$, the rank of solutions 1 through 7 is three, also. However, at $\Delta T = 0.004$, the rank is four due to the three metal-ligand species and the small absorbance of the free ligand at 440 mμ in solutions 6 and 7 (Figure 14).

The absorbance and error matrices for Series IV were 80 x 7 with the wavelength range the same as in previous series. The rank of three indicates three metal-ligand species, since the free ligand does not absorb in this series of solutions.

Matrix rank analysis indicates the presence of three tin(IV)-pyrocatechol violet complexes. The primary absorption peaks for these species occur at 610 mμ and at 550 mμ. The absorbance at 610 mμ occurs only for values of the ratio $C_{PCV}:C_{Sn}$ less than one indicating the possibility of polynuclear species.

The species number calculation was made on solutions 1 through 7 of Series I, 2 through 7 of Series II, and 1 through 7 of Series III and IV. The calculation tested each data set for linearity assuming one, two, and three absorbing species with nonconstant stoichiometry. Equations (19), (23), and (27) were used to calculate the X and Y absorbance functions for each case. The best straight line fits were calculated for each of 16 wavelengths for the one and two species cases. The wavelengths used were 660, 635, 610, 585, 560, 535, 510, 485, 460, 435, 410, 385, 360, 335, 310, and 285 mμ. Only six to eight of these lines are plotted in the following figures because of space limitations. The total number of lines for the three species model in each case is equal to the number of solutions being run. Only three or four lines will be plotted because of space limitations.

The results of the species number calculations are given in Figures 16, 17, and 18 for Series I, Figures 19, 20, and 21 for Series II, Figures 22, 23, and 24 for Series III, and Figures 25, 26, and 27 for Series IV. For each series the result is the same as obtained in the matrix rank analysis. The species number plots indicate three absorbing species in each series.

It is obvious by visual inspection of the species number plots which assumed model gives the best straight line for each series of solutions. The values of the goodness-of-fit parameter, SMIN, are of interest in verifying this conclusion. These values are given in Table XVI.

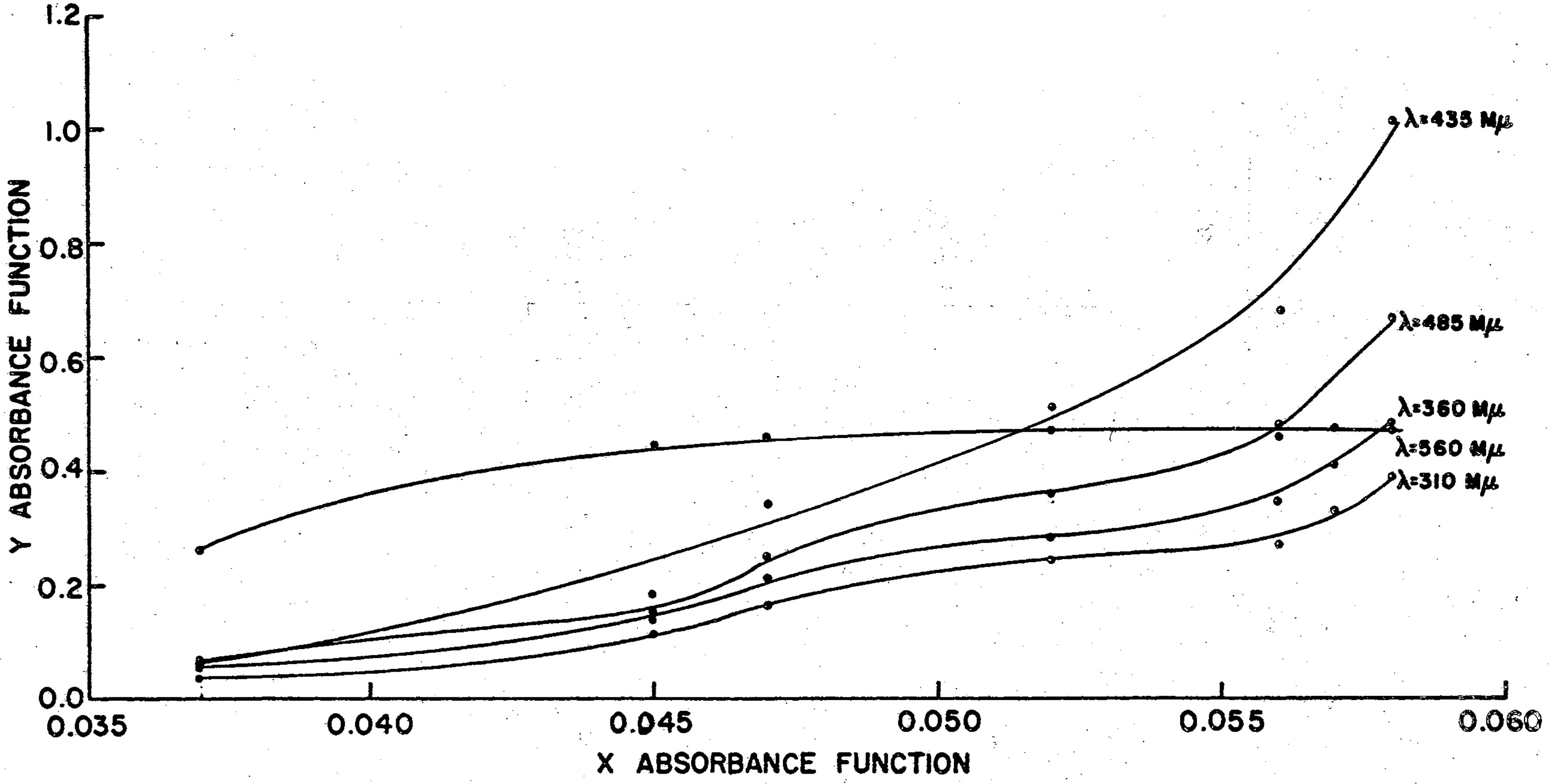


Figure 16. Species Number Plot Series I, One Absorbing Species

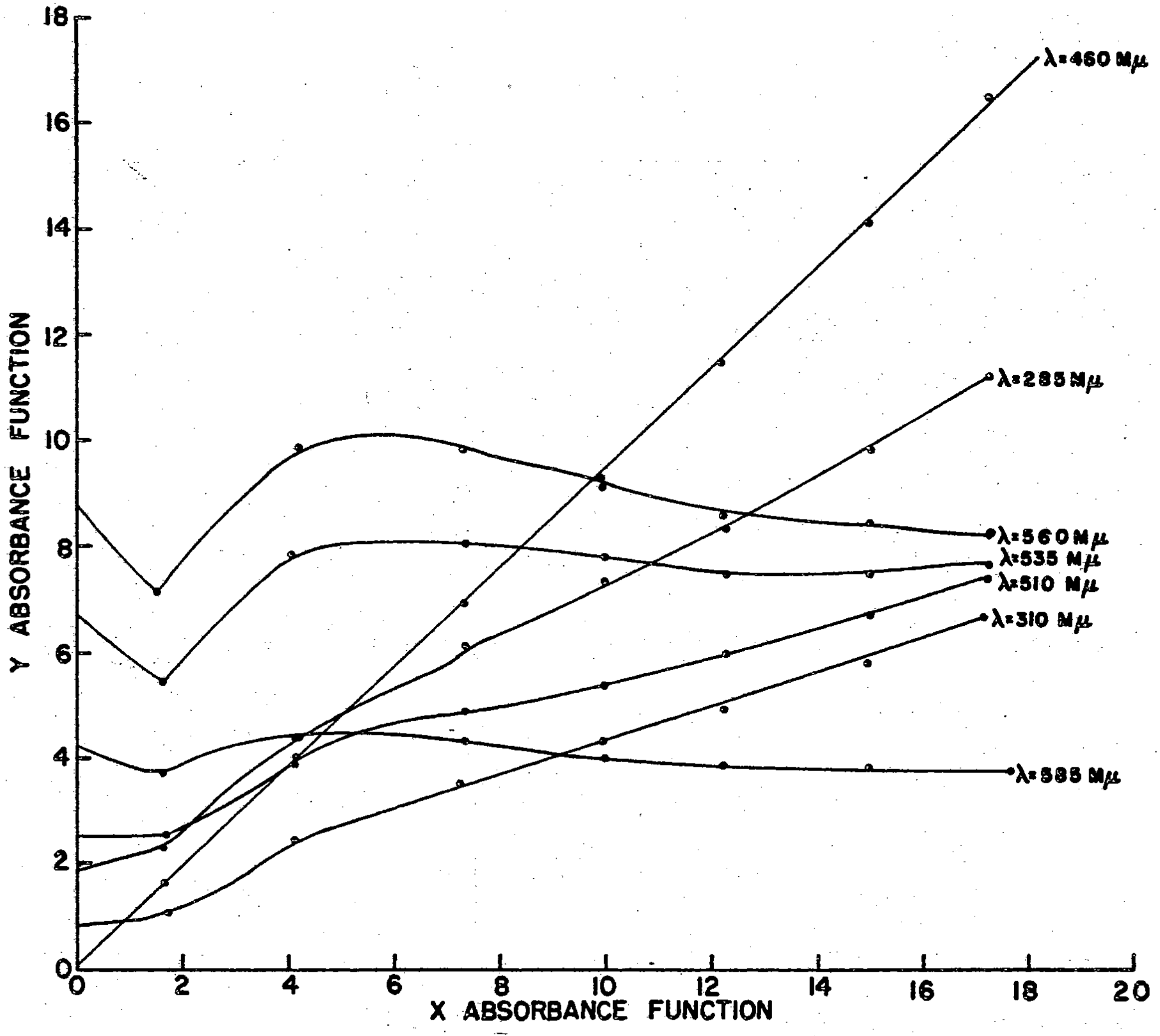


Figure 17. Species Number Plot Series I, Two Absorbing Species

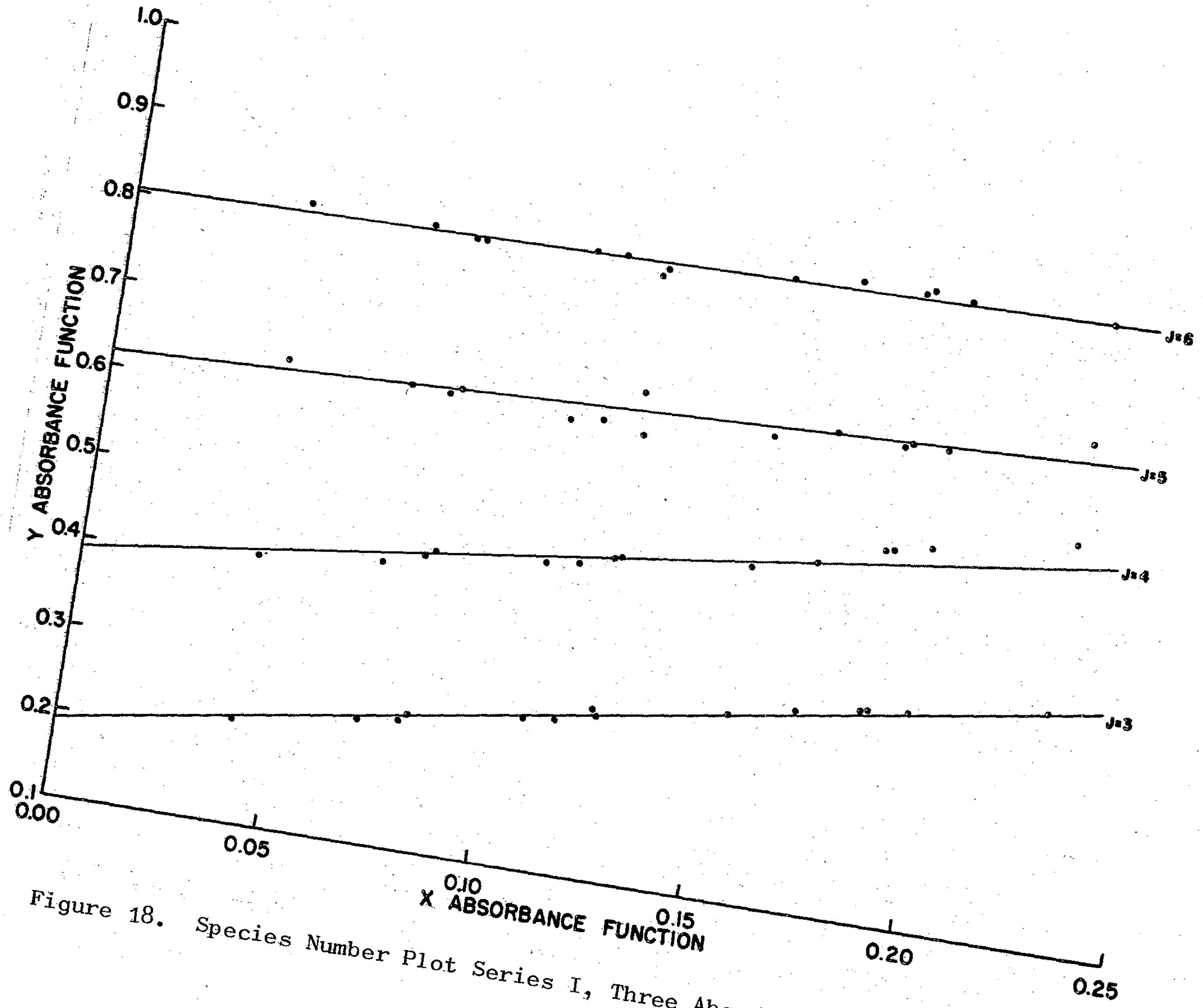


Figure 18. Species Number Plot Series I, Three Absorbing Species

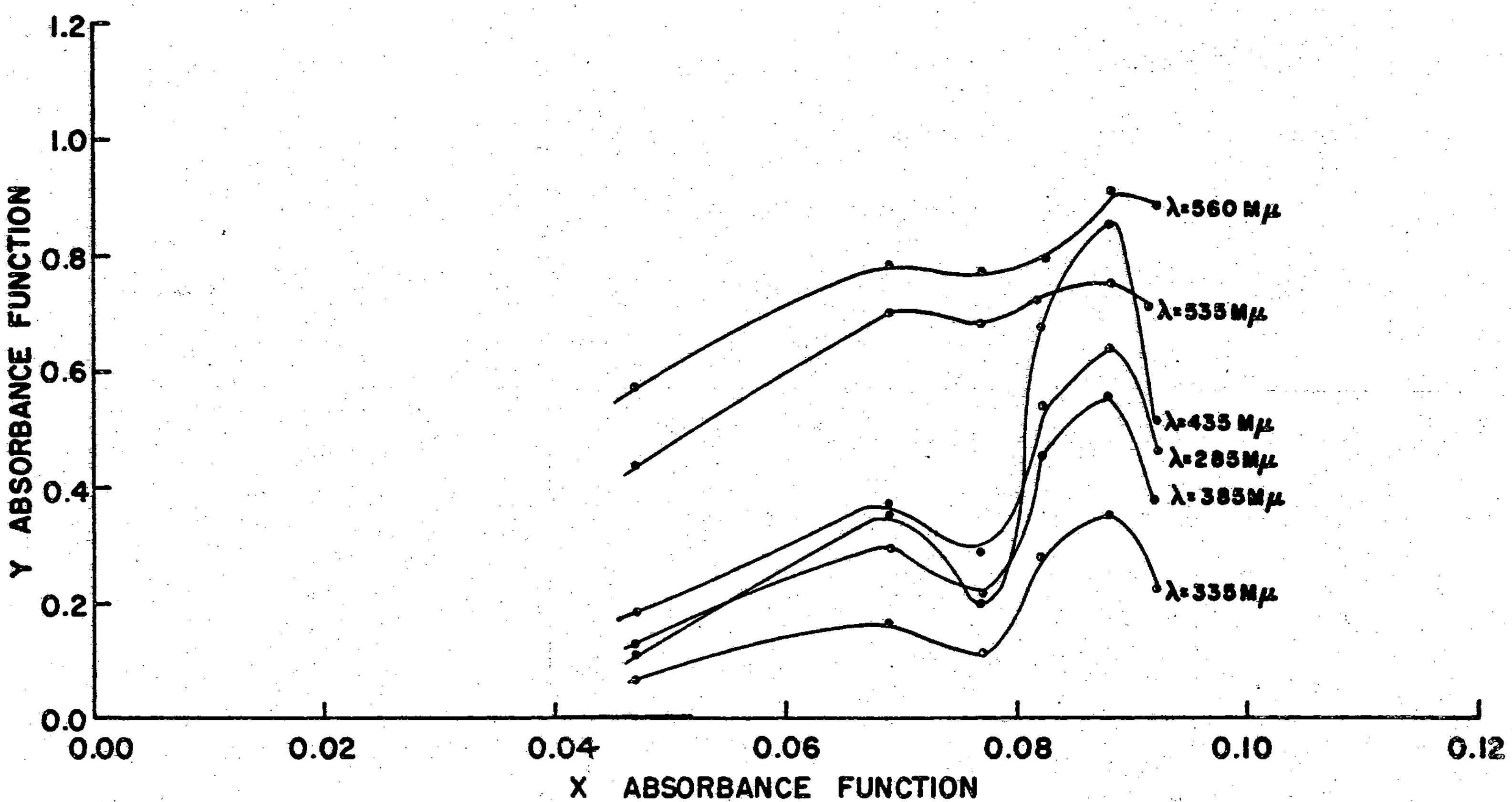


Figure 19. Species Number Plot Series II, One Absorbing Species

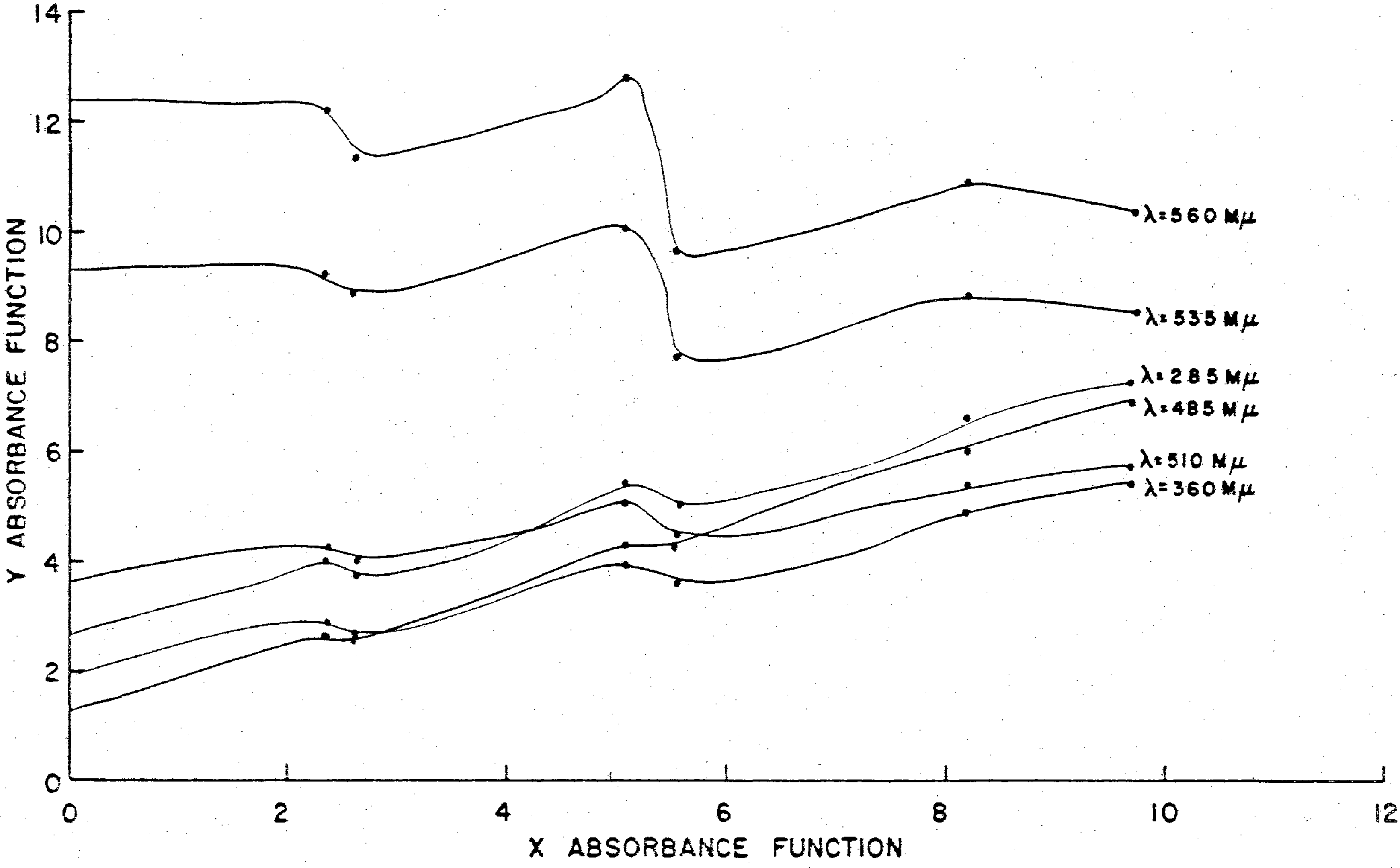


Figure 20. Species Number Plot Series II, Two Absorbing Species

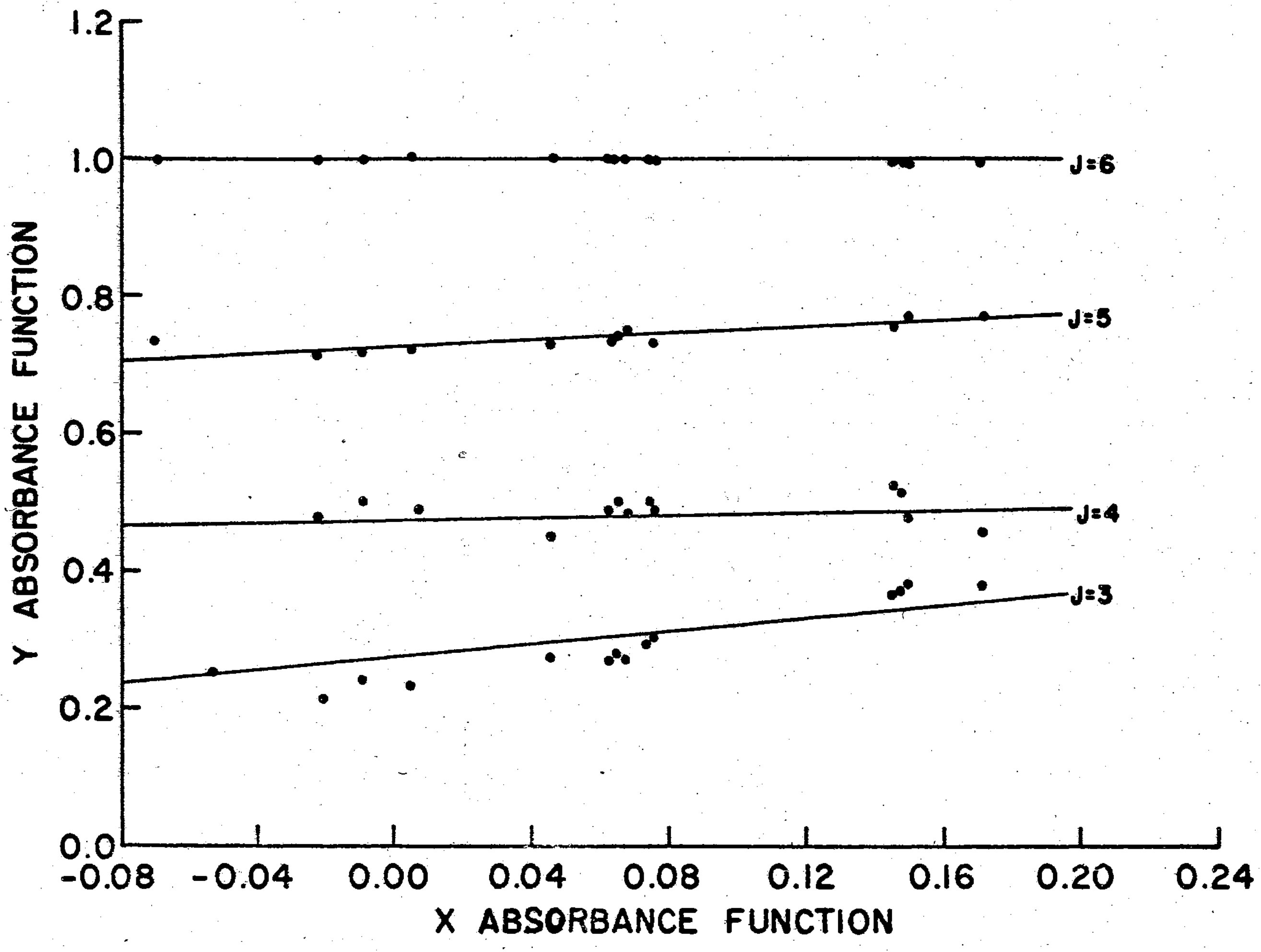


Figure 21. Species Number Plot Series II, Three Absorbing Species

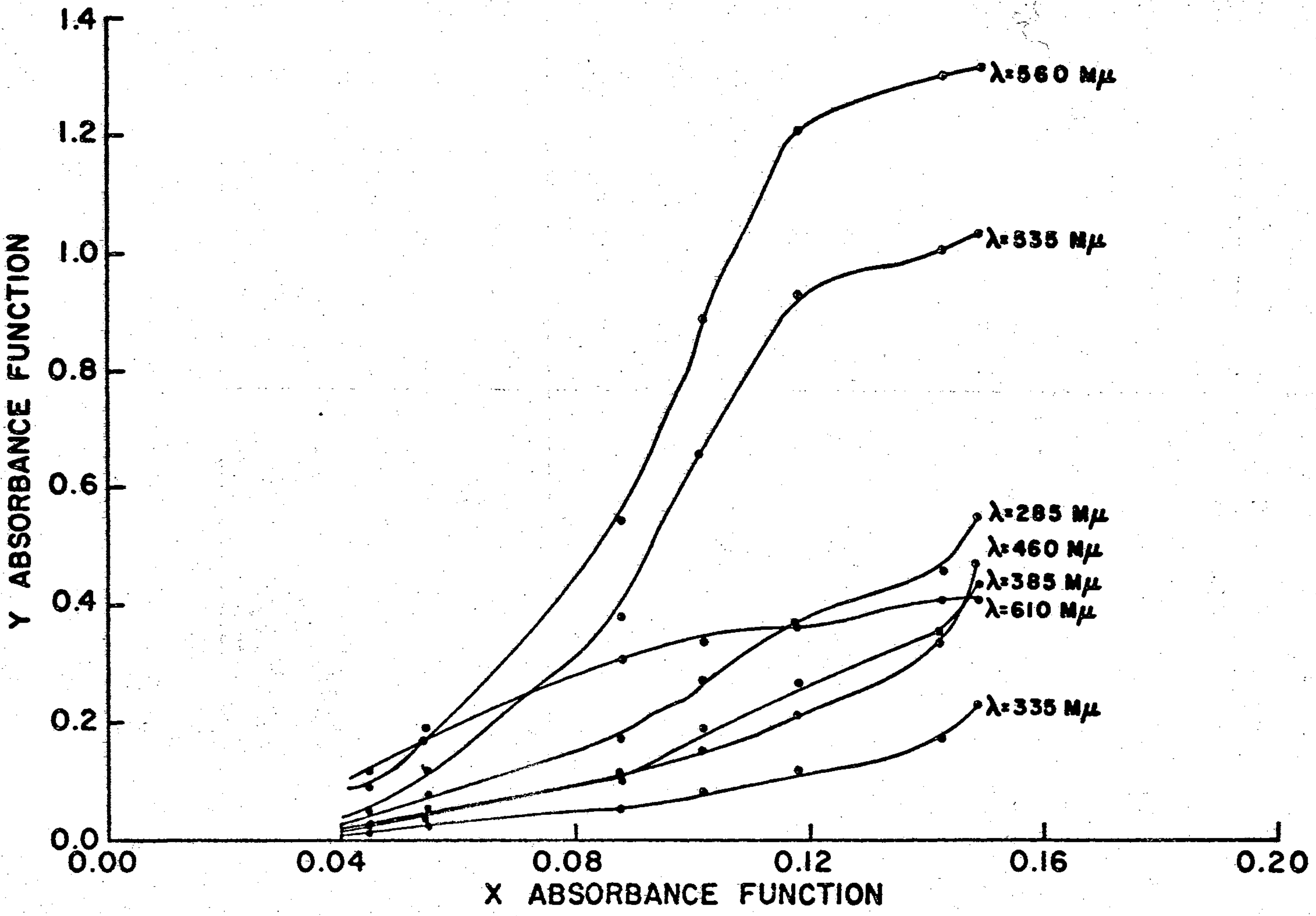


Figure 22. Species Number Plot Series III, One Absorbing Species

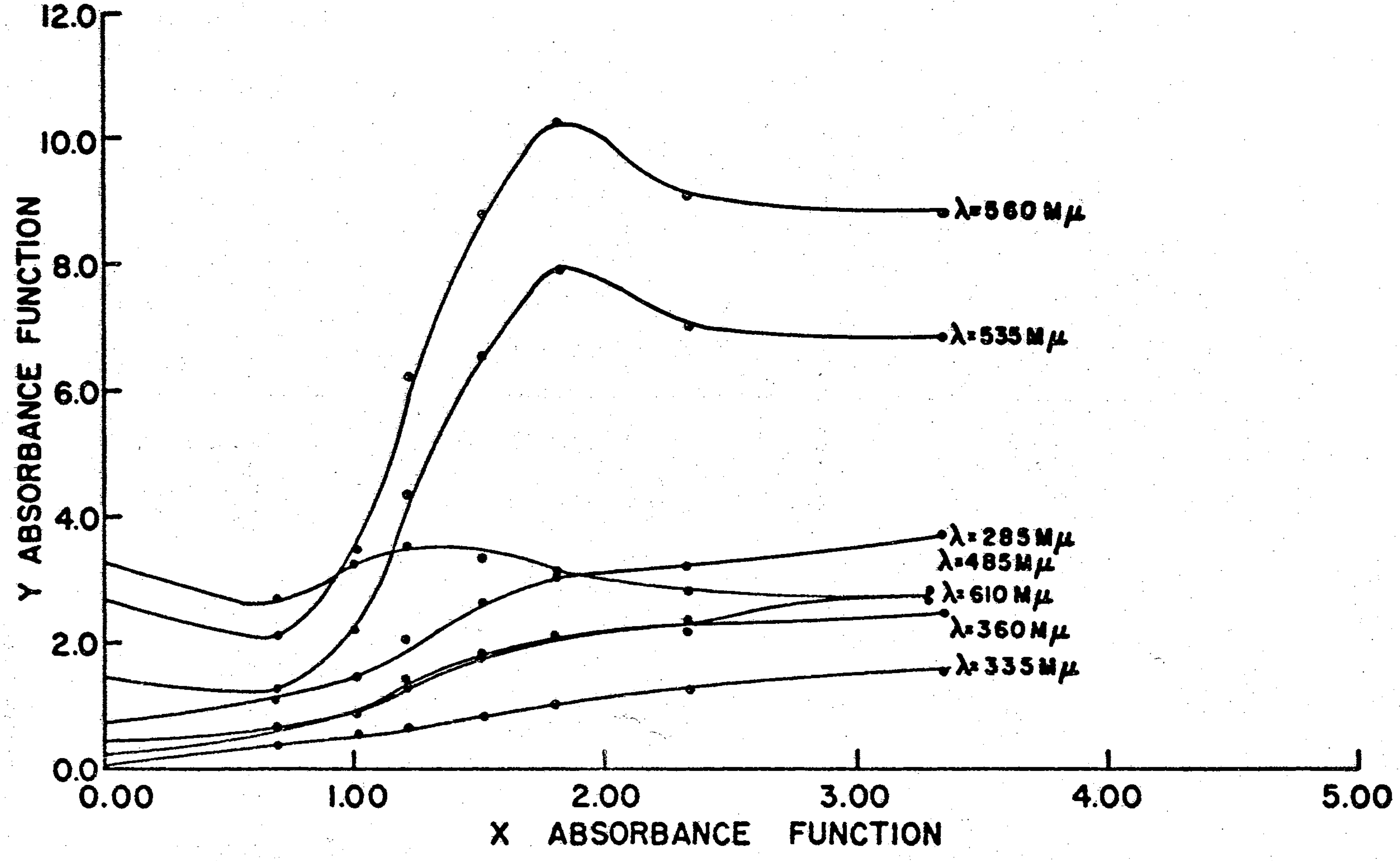


Figure 23. Species Number Plot Series III, Two Absorbing Species

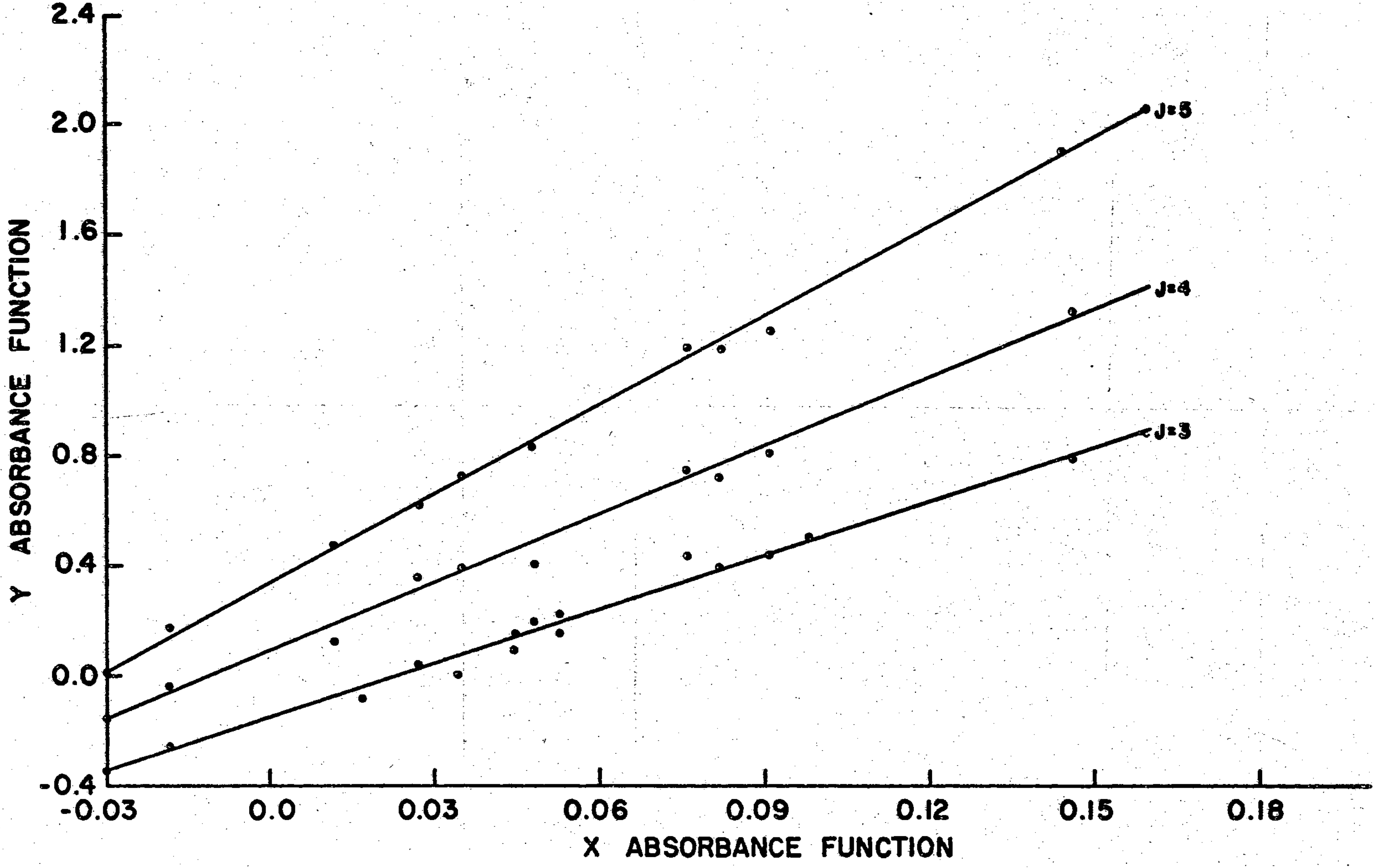


Figure 24. Species Number Plot Series III, Three Absorbing Species

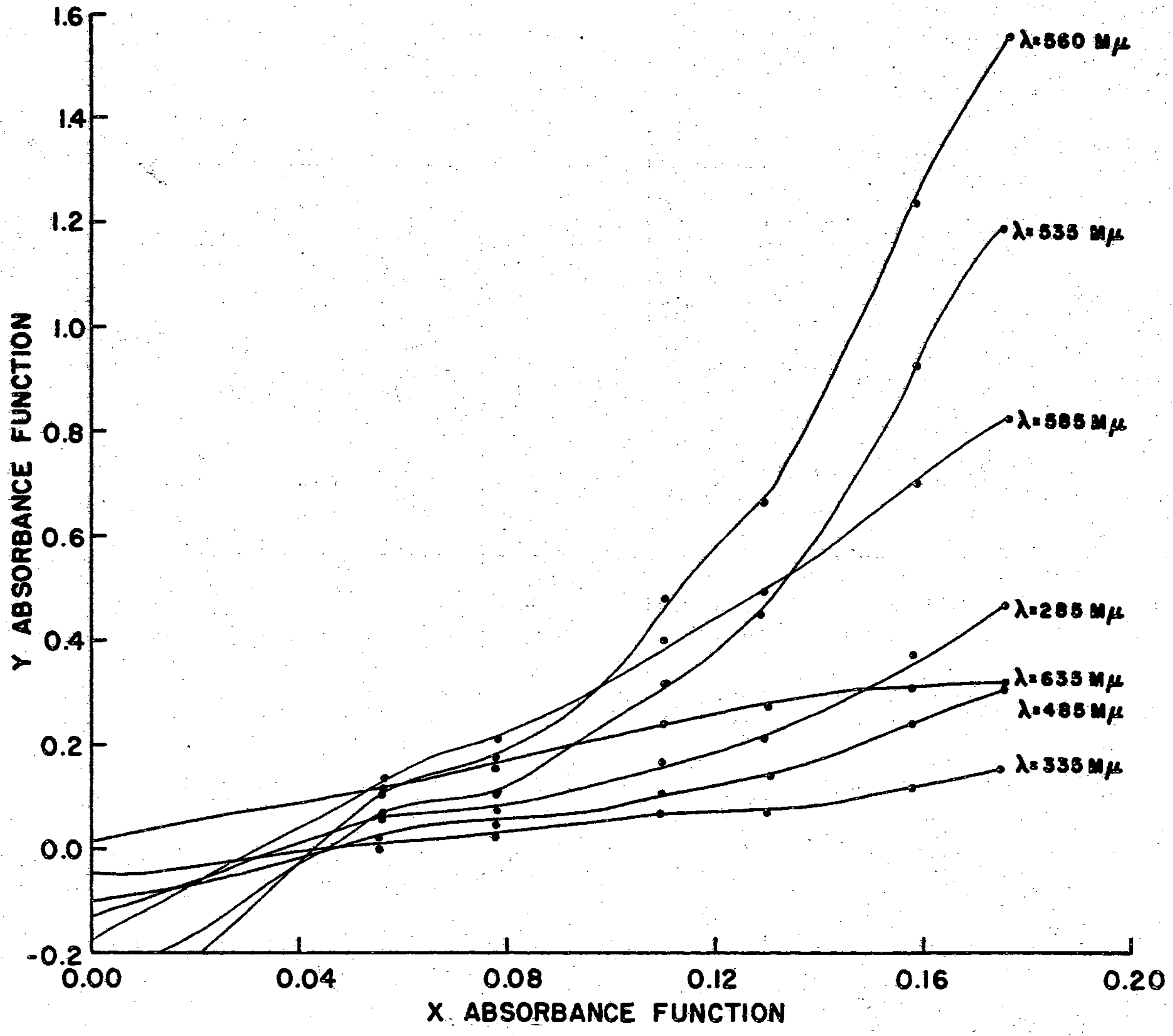


Figure 25. Species Number Plot Series IV, One Absorbing Species

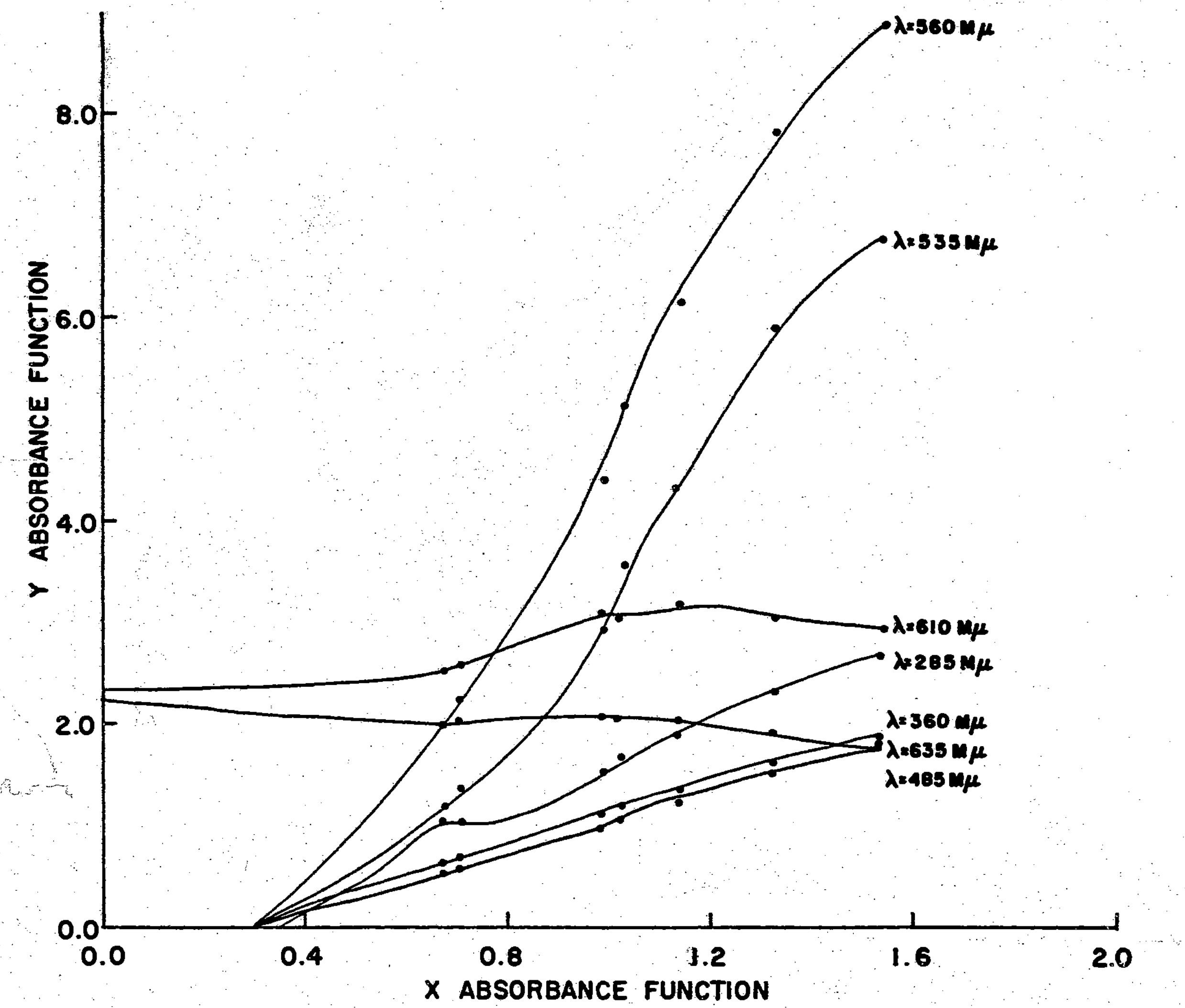


Figure 26. Species Number Plot Series IV, Two Absorbing Species

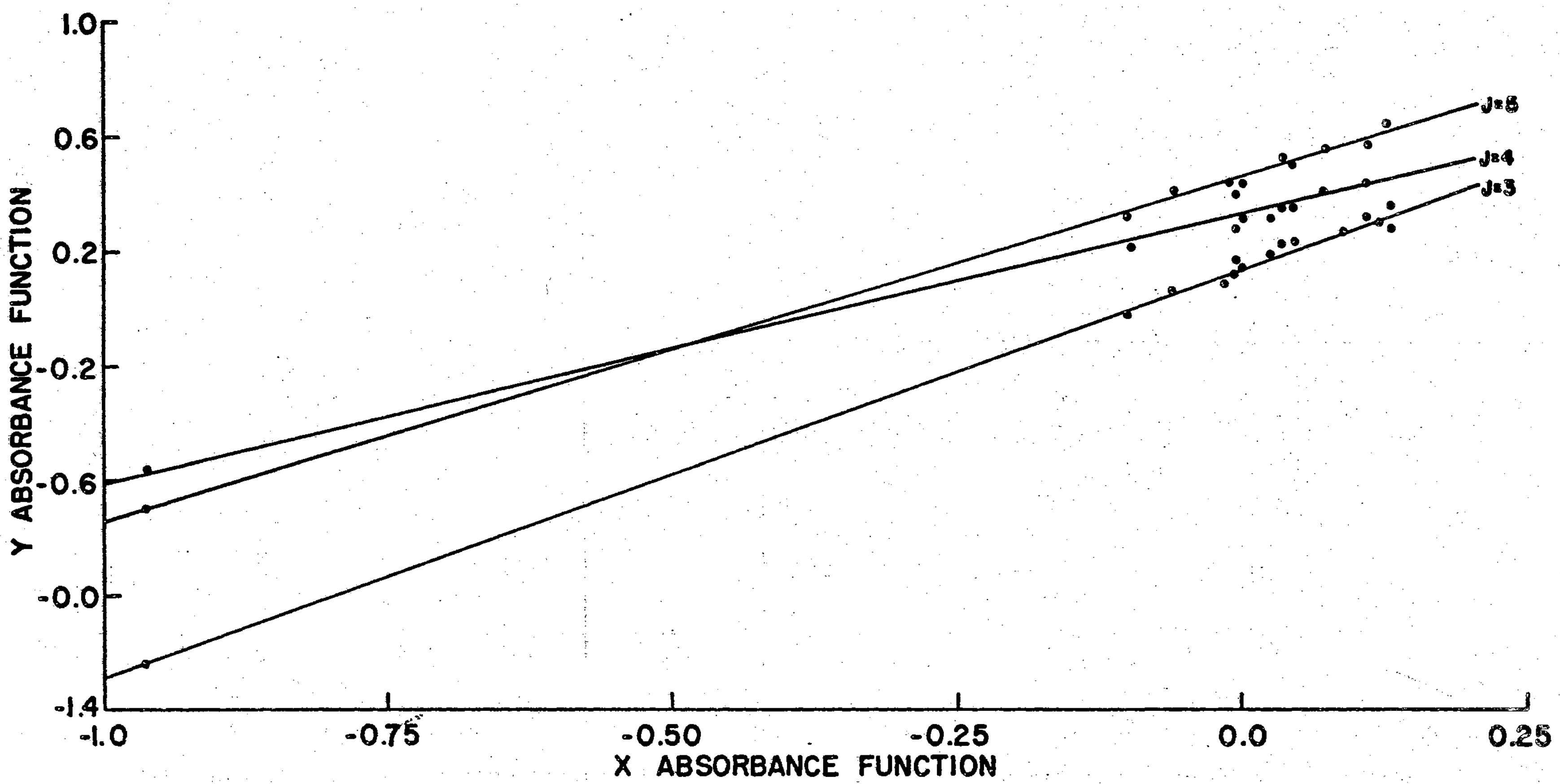


Figure 27. Species Number Plot Series IV, Three Absorbing Species

TABLE XVI

GOODNESS-OF-FIT PARAMETERS FOR SPECIES NUMBER CALCULATIONS

Model	SMIN Series I	Series II	Series III	Series IV
1 absorbing species	17.5 - 335.5	6.33 - 1163.4	25.01 - 261.07	15.73 - 286.88
2 absorbing species	0.078 - 1.38	0.19 - 1.70	0.01 - 7.03	0.002 - 0.109
3 absorbing species	$6.8 \times 10^{-5} - 1.4 \times 10^{-3}$	0.003 - 0.17	0.01 - 0.1	0.008 - 0.047

The results of the matrix rank analysis and the species number calculations indicate the presence of three tin(IV)-pyrocatechol violet complexes. When solutions having values of the ratio $C_{PCV}:C_{Sn}$ less than one are omitted from the matrix rank calculations, the rank is decreased by one. This species absorbs at 610 mμ. This indicates the possible presence of a polynuclear species absorbing at 610 mμ.

Nature of Absorbing Species

The mole-ratio method described by Yoe and Jones (9) is used to obtain information concerning the nature of the tin(IV)-pyrocatechol complexes in solution. Mole-ratio plots were made at 550 and 610 mμ for each series of solutions given in Tables VI, VII, VIII, and IX. These plots are shown in Figure 28. At 550 mμ the break in the mole-ratio plot for Series I occurs at a value of two for the ratio C_L/C_M. This corresponds to a complex of the composition ML_2. The ligand, H_3PV^-, is in excess for the last six solutions of Series I with the largest C_L/C_M ratio being 7. This indicates that ML_2 is the highest complex formed. The breaks in the mole-ratio plots range from two in Series I, one and one-half in Series II, near one in Series III, and no break in Series IV. The maximum ligand excess decreases from Series I through Series IV. The breaks in the mole-ratio plots indicate a mixture of ML and ML_2 present in solution.

The mole-ratio plots at 610 mμ break at a C_L/C_M value of one half indicating the presence of a dinuclear complex M_2L. The plots of each of the four series has a distinct break at $C_L/C_M = ½$.

The Holme-Langmyhr method for determining the values of m and n in the complex M_mL_n was used to check the probable existence of a

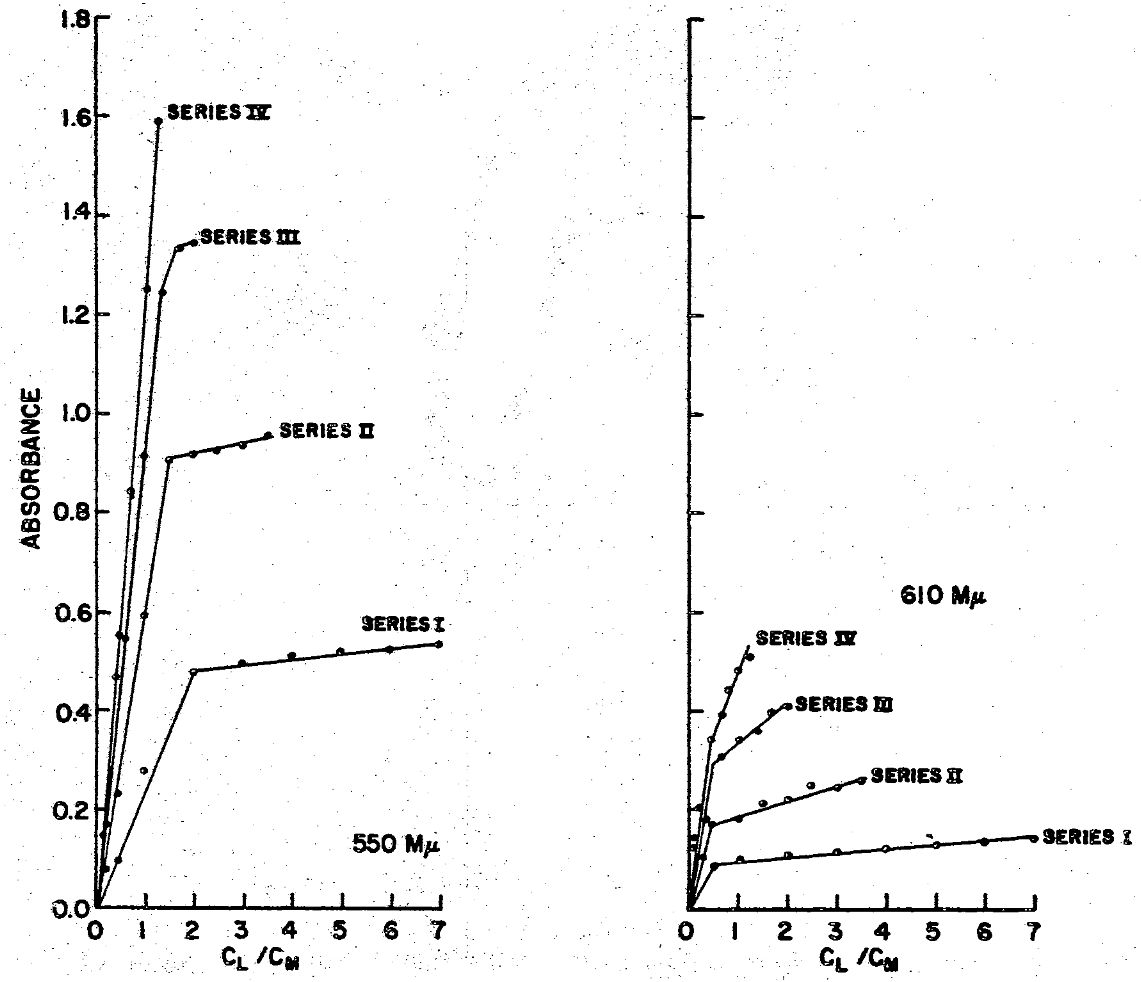


Figure 28. Mole Ratio Plots

dinuclear tin(IV)-pyrocatechol violet complex. The equations used were derived by Holme and Langmyhr (15) and have been used in a similar study by Thomson (68). The ratio n/m for a tin(IV)-pyrocatechol violet complex (M_mL_n) at 610 mμ was obtained by plotting

$$\frac{1}{(C_L - n/mC_M)^{n/m}} \times 10^{-4n/m} \quad \text{versus } 1/A$$

for various values of the ratio n/m. The necessary absorbance values were obtained from Series I, II, and III. The correct value of n/m gives a straight line plot. The results are shown in Figure 29. The only straight line obtained was for n/m = ½ and a value of $A_0^m = 5.83$ was obtained by extrapolation. A_0^m is an upper absorbance limit occurring if the concentration of reactant M is held constant and the concentration of L is increased until the concentration of the complex approaches an upper limit.

$$\lim_{C_L \to \infty} [M_mL_n] = C_M / m$$

The value of n for a tin(IV)-pyrocatechol violet complex (M_mL_n) at 610 mμ is obtained from a plot of

$$\frac{1}{\left(C_L - \frac{nA}{mA_0^m} C_M\right)^n} \times 10^{-4n} \quad \text{versus } 1/A \quad .$$

Various values of n were tried, with the correct value yielding a straight line as shown in Figure 30. The best straight line obtained was for n = 1.

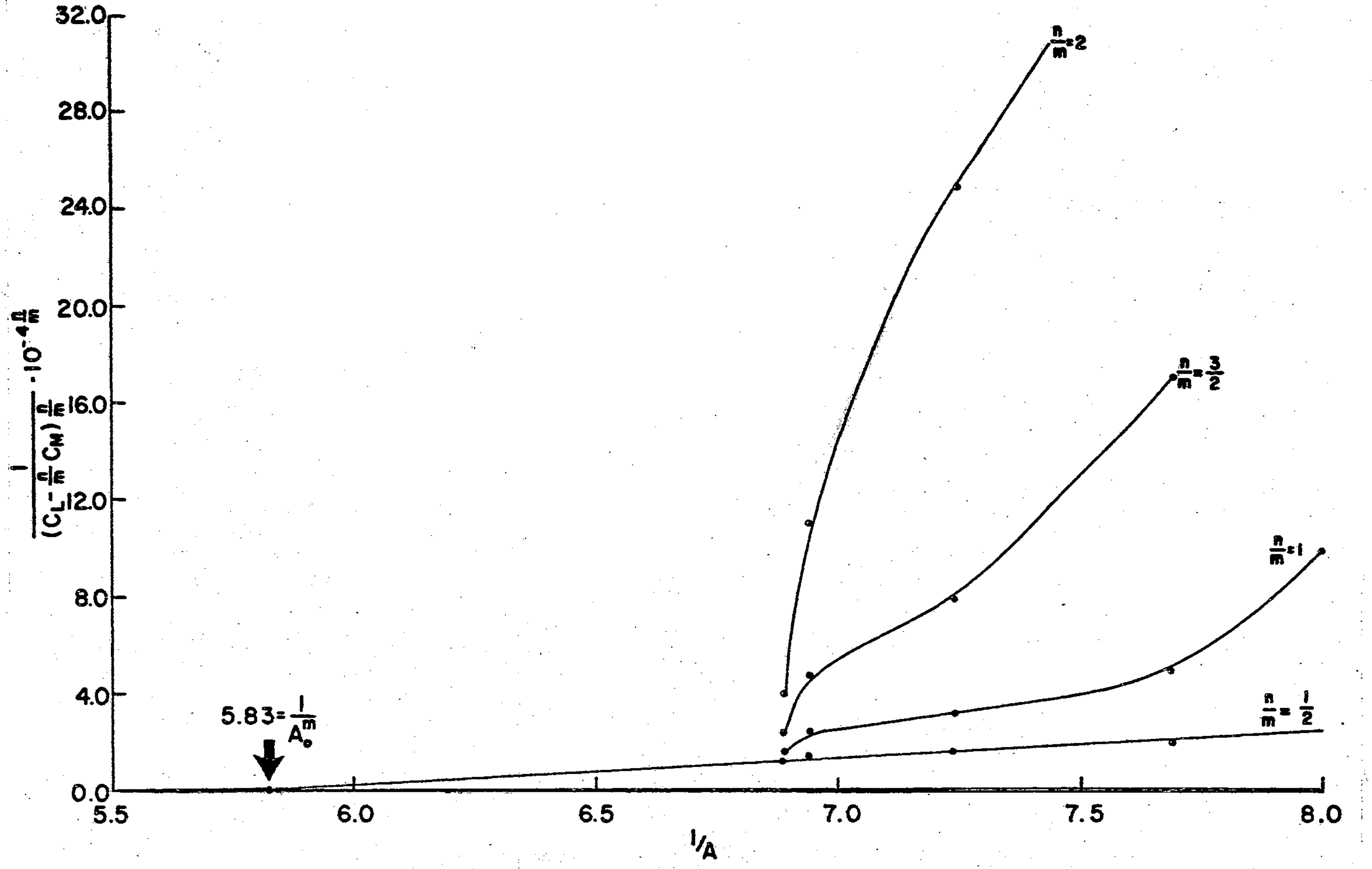


Figure 29. Ratio n/m for a Complex of Tin(IV)-Pyrocatechol Violet at 610 mμ

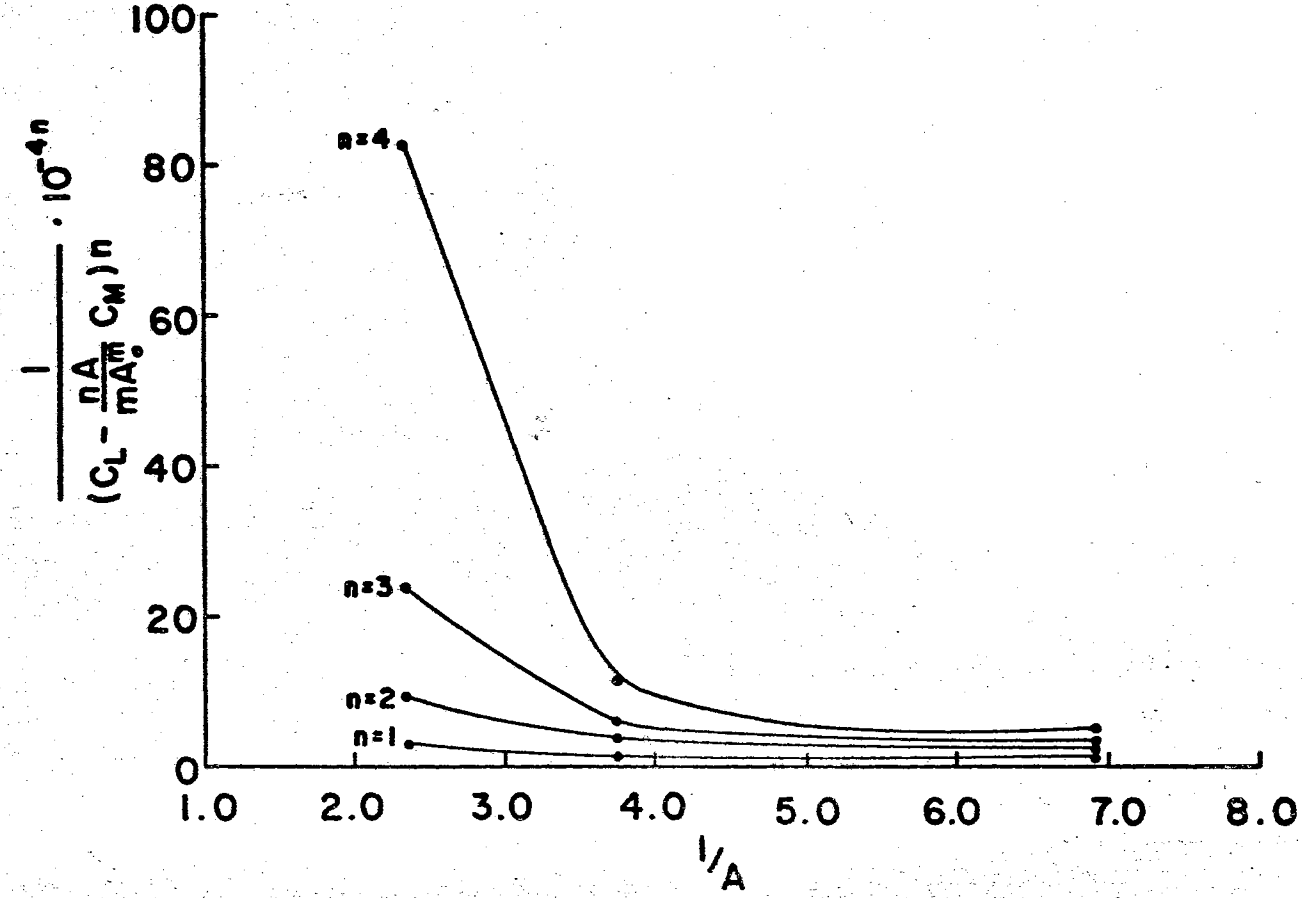


Figure 30. Coefficient n for a Complex of Tin(IV)-Pyrocatechol Violet at 610 mμ

The results of the mole-ratio method and the Holme-Langmyhr method indicate the presence of a dinuclear tin(IV)-pyrocatechol violet complex in solutions of low C_L/C_M ratios. The presence of 1:1 and 1:2 mononuclear complexes is indicated by the mole-ratio plots at 550 mμ. These results are in agreement with earlier results of the matrix rank analysis and the species number calculation.

Stabilities of Tin(IV)-Pyrocatechol Violet Complexes

The method of corresponding solutions cannot be used to interpret spectrophotometric data if polynuclear complexes exist in solution. However, the method can be used to check for the presence of such species as described earlier.

The corresponding solutions plot program was run on the absorbance data obtained from the spectra given in Figures 12, 13, 14, and 15. Corresponding solution plots similar to Figure 3 were obtained in the wavelength range from 515 to 590 mμ. No well behaved curves were obtained in the region of 610 mμ.

The corresponding solutions $\bar{n}$, $[L]$ program was run at 535, 550, 565, and 580 mμ using the E values calculated in the corresponding solutions plot program as input data. The $\bar{n}$, $[L]$ values obtained are given in Table XVII.

Different $\bar{n}$, $[L]$ curves were obtained at each wavelength, which is the result expected if polynuclear species are present. All wavelengths used were associated with the absorption at 550 mμ. If corresponding solution plots could have been made at wavelengths associated with other absorption bands, the differences in $\bar{n}$, $[L]$ values probably would have been even greater. The conclusion is that

TABLE XVII

FORMATION FUNCTION DATA

$\bar{n}$	535 mμ $[L] \times 10^{6}$	$\bar{n}$	550 mμ $[L] \times 10^{6}$	$\bar{n}$	565 mμ $[L] \times 10^{6}$	$\bar{n}$	585 mμ $[L] \times 10^{6}$
0.4801	0.2313	0.4809	0.4056	0.4879	0.8435	0.4825	1.8291
0.5885	0.6376	0.5853	0.6437	0.5949	1.5317	0.5849	3.8787
0.6913	0.9384	0.6897	0.7728	0.6961	2.1451	0.6666	4.8613
0.7888	1.2155	0.7917	0.8882	0.7988	2.6955	0.7623	5.7423
0.8801	1.5634	0.8868	1.1135	0.8874	2.9585	0.8951	6.3249
0.9950	2.2299	0.9954	1.6514	0.9610	2.9489	0.9791	8.5743
1.1283	2.9720	1.1469	2.3345	1.1310	4.4068	-	-

at least one polynuclear species is present and, therefore, some method other than corresponding solutions must be used to calculate the stability constants.

The stability constants of the tin(IV)-pyrocatechol violet complexes were determined from the spectra of the solutions given in Tables VI, VII, VIII, and IX using the pit-mapping program. The concentrations of each species in solution and the molar extinction coefficients of all tin(IV)-pyrocatechol violet complexes were also calculated. The spectra of the solutions between 660 and 265 mμ, the total pyrocatechol violet and tin(IV) concentrations, and the solution pH's were used as the primary input data for each series of solutions. The initial value of DEC was 0.10 in each case. Initial estimates of the stability constants were read in also.

Solutions 2 through 7 of Series II have $C_{PCV}:C_{Sn}$ ratios equal to or greater than one and the rank is three. Since the free ligand, H_3PV^-, contributes a rank of one, the number of metal-ligand species is two. The pit-mapping calculation was performed on the spectra of these six solutions using three different models:

$$ML \text{ and } ML_2$$

$$ML \text{ and } ML_3$$

$$ML_2 \text{ and } ML_3 \ .$$

Only the model assuming ML and ML_2 ($Sn(H_2PV)^{2+}$ and $Sn(H_2PV)_2$) was successful. The initial estimates for PKP1 and PKP2 ($-\log \beta_{11}$ and $-\log \beta_{12}$) were -8.5 and -15.0. Six repetitions were required for convergence. The following results were obtained:

$$\log \beta_{11} = 7.797 \pm 0.312$$

$$\log \beta_{12} = 14.741 \pm 0.321$$

$$\mathrm{UMIN} = 0.342 \ .$$

The agreement between the experimental and calculated spectra was excellent.

The pit-mapping calculation was performed on solutions 0 through 7 of Series I, solutions 0 through 7 of Series II, and solutions 1 through 7 of Series III and IV. From the matrix rank and species number results, it is known that each of the above series of solutions contain three tin(IV)-pyrocatechol violet complexes. The results of the mole-ratio method, the Holme-Langmyhr method, and the previous pit-mapping calculations indicate one polynuclear (probably dinuclear) and two mononuclear (probably ML and ML_2) complexes. For these reasons three species models were used in subroutine EQUIL for all of the above sets of solutions. The models tried were:

ML, ML_2, ML_3

M_2L, ML, ML_2

M_2L_2, ML, ML_2

M_2L_3, ML, ML_2

M_2L_4, ML, ML_2 .

With the exception of the ML, ML_2, and ML_3 case, all models tried contained one polynuclear and two mononuclear complexes. The only model which gave meaningful results was the M_2L, ML, and ML_2 model described earlier. All other models were eliminated because they gave large error-square sums (10^{15} - 10^{18}), negative molar extinction coefficients, and poor agreement between experimental and calculated spectra.

The model M_2L, ML, and ML_2, described in detail earlier, was tried for each series of solutions. In each case convergence was obtained. Good fits of the spectra, small error-square sums, and stability constants with small standard deviations were obtained. The input estimates for PKP1, PKP2, and PKP3 ($-\log \beta_{11}$, $-\log \beta_{12}$, and $-\log \beta_{21}$, respectively) were -7.800, -14.740, and -13.000. The initial value for DEC was 0.10. A maximum of five repetitions was required for convergence in each series. The results obtained are given in Table XVIII. The calculated molar extinction coefficients for $Sn(H_2PV)^{2+}$, $Sn(H_2PV)_2$, and $Sn_2(H_2PV)^{6+}$ are plotted in Figure 31 and are tabulated in Table XIX. The calculated concentrations of all tin(IV) species are plotted in Figures 32, 33, 34, and 35 for Series I, II, III, and IV, respectively.

TABLE XVIII

FORMATION CONSTANTS OF TIN (IV) - PYROCATECHOL VIOLET COMPLEXES

	Series I	Series II	Series III	Series IV	Average	Std. Dev.
$\log\beta_{11}$	7.649	7.765	7.970	7.823	7.801	0.133
$\log\beta_{12}$	14.594	14.758	15.282	14.963	14.899	0.297
$\log\beta_{21}$	13.210	12.451	13.136	12.889	12.922	0.342
UMIN	0.132	0.337	0.184	0.193		

TABLE XIX

MOLAR EXTINCTION COEFFICIENTS

Wave-length mμ	HPV^{3-}	H_2PV^{2-}	H_3PV^-	H_4PV	$Sn(H_2PV)^{2+}$	$Sn(H_2PV)_2$	$Sn_2(H_2PV)^{6+}$
660					3356	8986	7010
655					4066	10240	8785
650					4716	11230	10420
645					5421	12080	12550
640					6126	12460	14540
635					6877	13390	16490
630					7638	14180	18400
625					8603	14940	19630
620	1929	23490	337	1956	9475	16800	21080
615	3071	29400	333	2960	10540	18210	22100
610	3966	34860	320	4330	11450	20040	22720
605	4632	39330	298	6280	12370	22380	23010
600	5718	41760	260	8943	13360	24830	22980
595	6615	42260	223	12390	14420	28050	22810
590	6884	41390	186	16600	15770	31870	22520
585	6528	39770	150	21680	17350	37210	21960
580	6511	37900	111	27450	19610	44150	20760
575	6017	36000	89	32900	22450	52940	19460
570	6238	34330	89	37610	25990	61310	17720
565	6230	32660	119	41380	29540	69720	16140
560	6089	31090	176	43590	32430	76960	14130
555	6482	29260	289	44070	33730	79620	12790
550	6570	27430	471	43040	33160	78140	11140
545	6554	25590	712	41000	31150	73730	9801
540	6574	23640	1037	38190	28030	67640	8177
535	6745	21610	1435	35000	24350	59630	6855
530	6867	19820	1926	31670	20620	50290	5863
525	6943	18060	2503	28470	17210	41260	5603
520	7135	16510	3177	25230	14400	33670	4752
515	7126	15080	3951	21970	12160	27740	5146
510	7484	13640	4829	18790	10520	22690	4888
505	7948	12100	5813	15780	9170	19180	4800
500	7997	10870	6902	13150	8046	16150	5044
495	8483	9402	8036	10750	7126	13090	4922
490	9014	8122	9253	8660	6470	10220	4962
485	9477	6839	10480	7147	5925	8619	5170
480	10100	5624	11780	5717	5564	6884	5258
475	10090	4792	12900	4903	5245	5866	5587
470	10960	3575	14050	4190	4979	4974	5633
465	11220	2711	15110	3529	4818	3946	5934
460	11580	1861	15980	3239	4663	3062	6083
455	11640	1390	16660	3072	4542	2512	6156
450	12230	579	17160	2773	4474	2285	6230
445	12260	383	17420	2756	4392	2174	6423

TABLE XIX (Continued)

Wave-length mμ	HPV^{3-}	H_2PV^{2-}	H_3PV^-	H_4PV	$Sn(H_2PV)^{2+}$	$Sn(H_2PV)_2$	$Sn_2(H_2PV)_2^{6+}$
440	12250	377	17490	2682	4454	2286	6519
435	11730	861	17260	2807	4547	2746	6438
430	11360	1499	16860	2780	4765	3670	6426
425	10950	2035	16240	2956	5077	4655	6330
420	10100	2870	15450	2949	5369	5724	5866
415	9907	3207	14520	3240	5509	6572	5505
410	9453	3595	13530	3351	5572	7430	5209
405	9481	3645	12520	3566	5602	7987	4887
400	9017	4037	11540	3824	5598	9023	4356
395	8633	4370	10570	4188	5698	9915	4080
390	8464	4514	9669	4767	5961	11330	3812
385	8229	4669	8930	5247	6441	13010	3760
380	8287	4681	8236	5932	7082	14780	3962
375	8207	4755	7701	6472	7606	15800	4561
370	8376	4574	7319	6679	7750	15820	5021
365	8244	4495	7007	6425	7353	14280	5333
360	8495	4126	6785	6058	6350	12100	5237
355	8541	3883	6646	5359	5127	9518	4251
350	8399	3664	6571	4702	4130	7335	3839
345	8524	3231	6503	3741	3347	5695	3215
340	8340	3087	6438	3056	2852	4817	3098
335	8558	2945	6384	2647	2714	5240	2981
330	8614	3185	6315	2581	3979	5798	3165
325	8813	3675	6283	2847	3505	6545	3391
320	9290	4534	6302	3438	3896	7290	3909
315	10160	5947	6361	3933	4307	7968	4139
310	10930	7735	6442	4036	5011	9208	4913
305	11390	9615	5662	3997	6090	12010	5665
300	11580	10920	6796	3966	7983	16350	6452
295	11220	11270	7215	4829	9866	20610	7354
290	11030	10340	8160	6984	10220	20560	7811
285	10720	8927	9641	8880	9251	17940	7928
280	10650	7198	10870	8739	8419	15460	7564
275	10400	5512	10860	8100	7663	15010	7178
270	9504	4482	9762	7449	6968	14220	6764
265	9548	3400	8279	7112	6622	14680	6422
260	8232	4045	6899	7100			

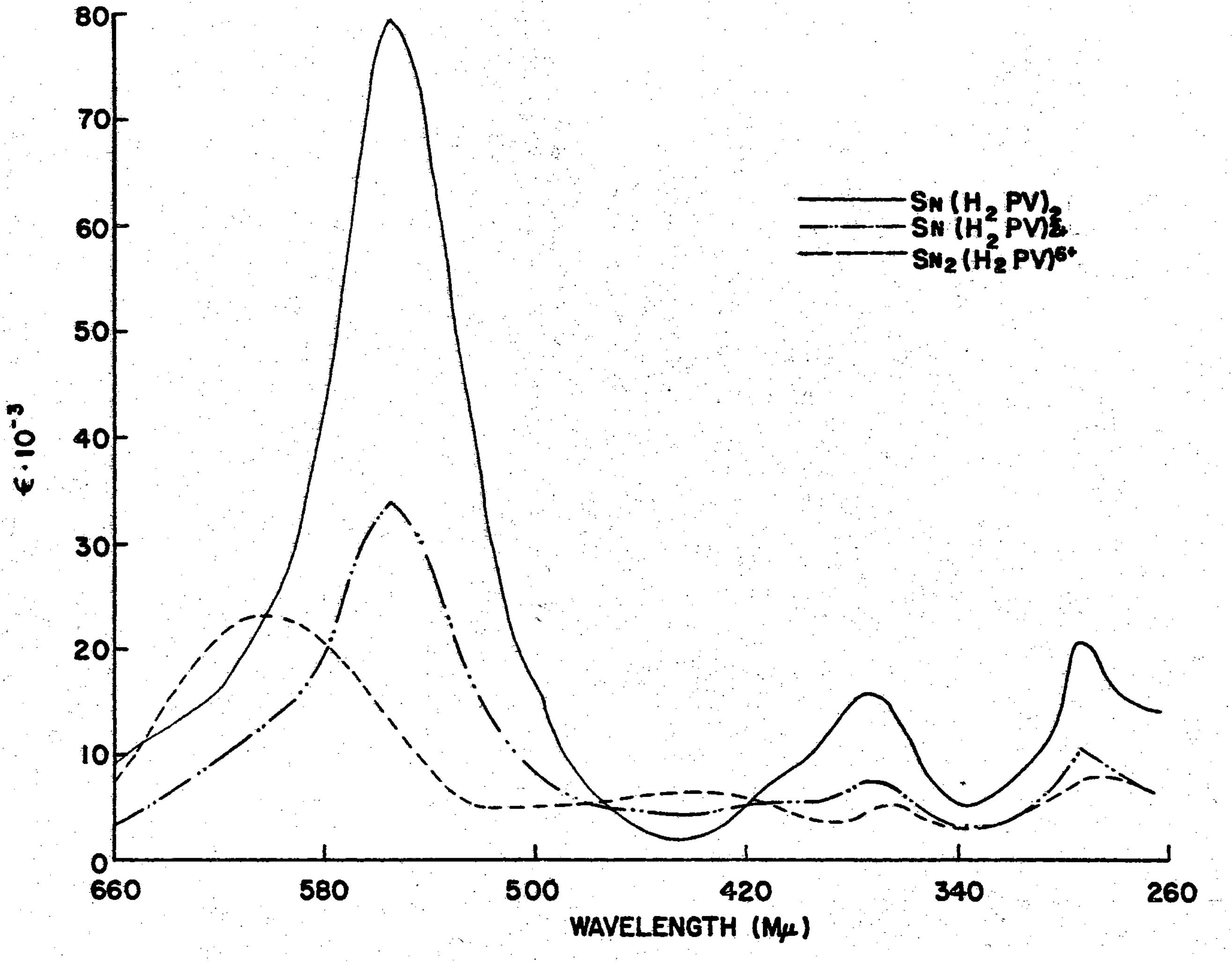


Figure 31. Molar Extinction Coefficients for Tin(IV)-Pyrocatechol Violet Complexes

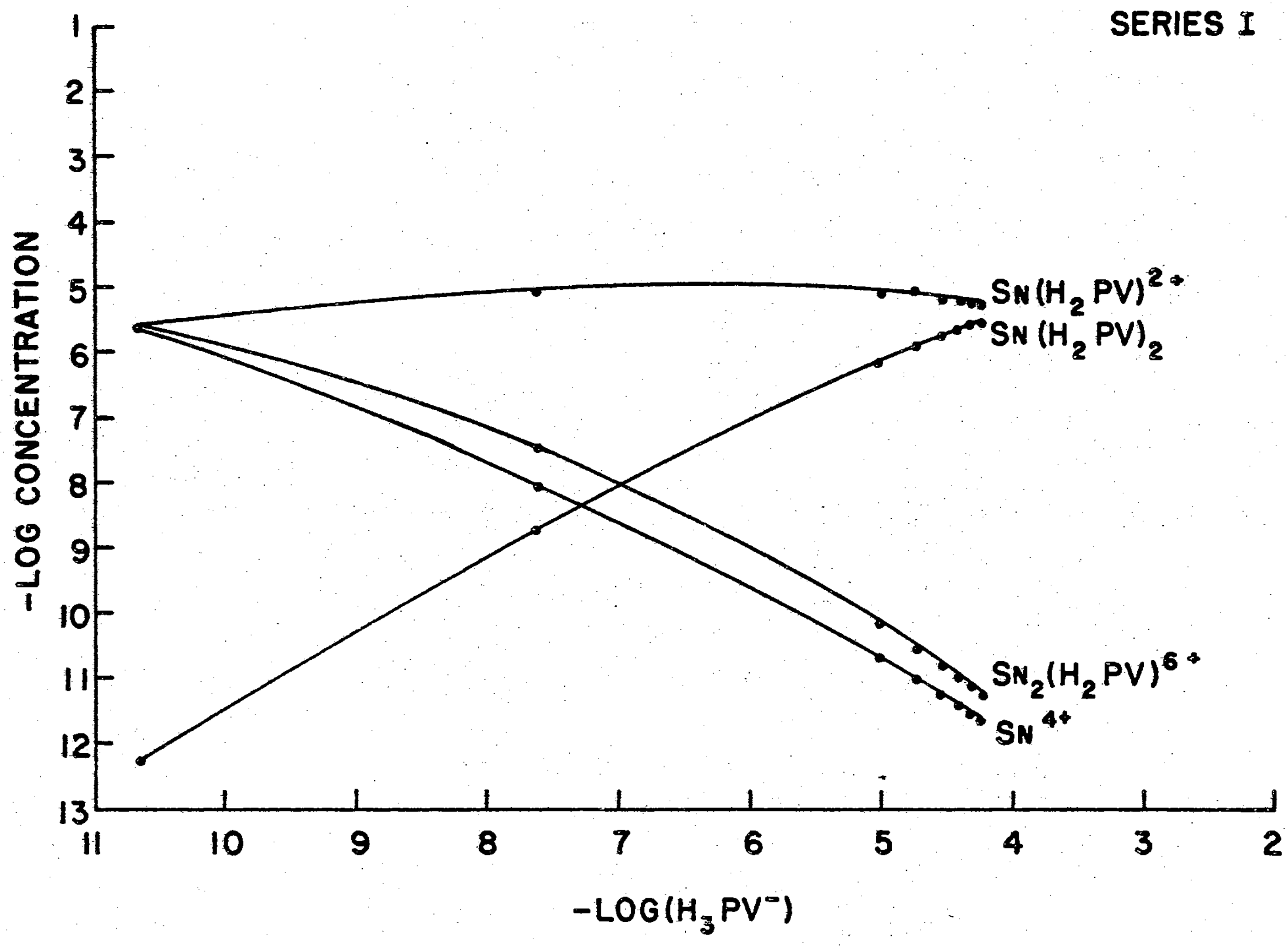


Figure 32. Concentration of Species, Series I

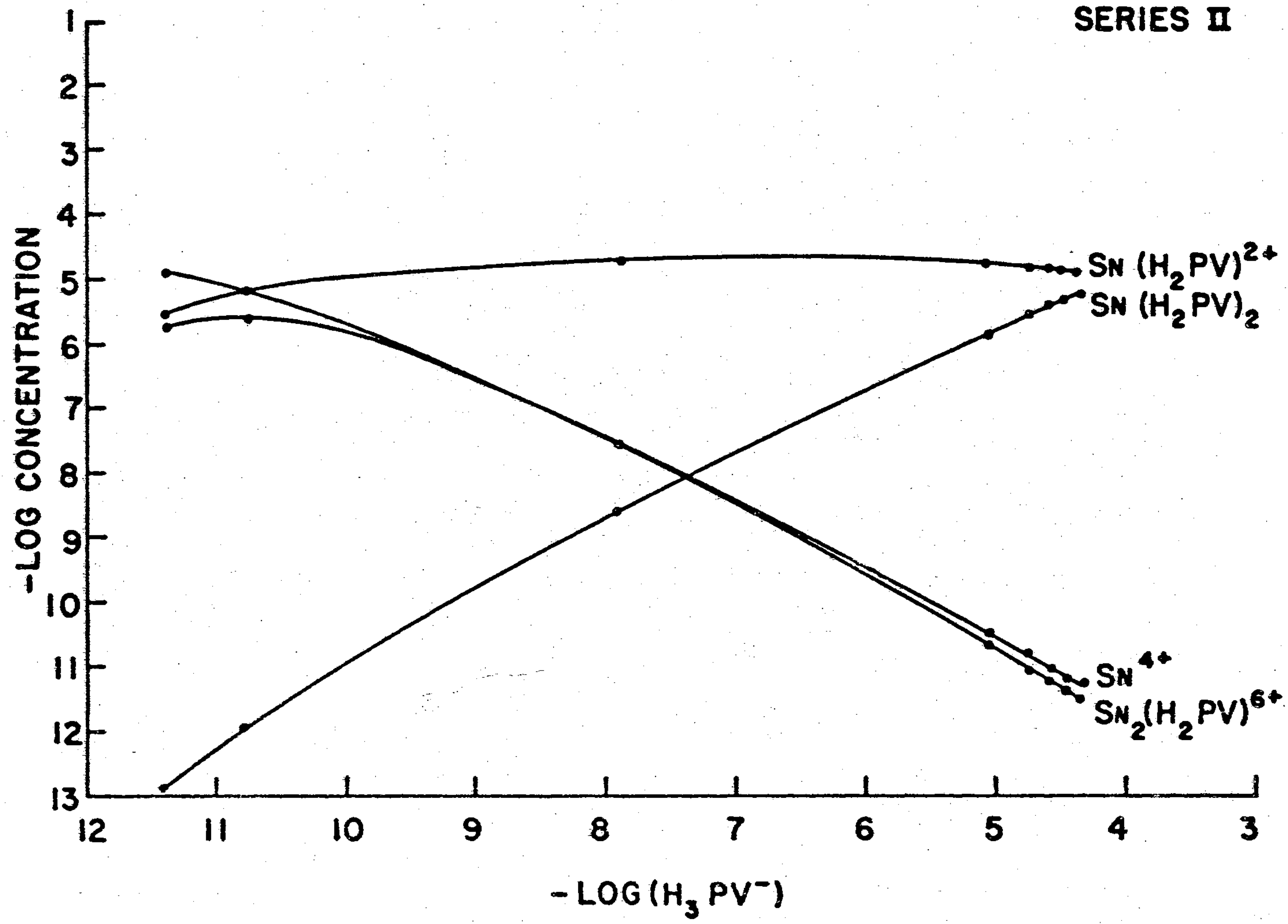


Figure 33. Concentration of Species, Series II

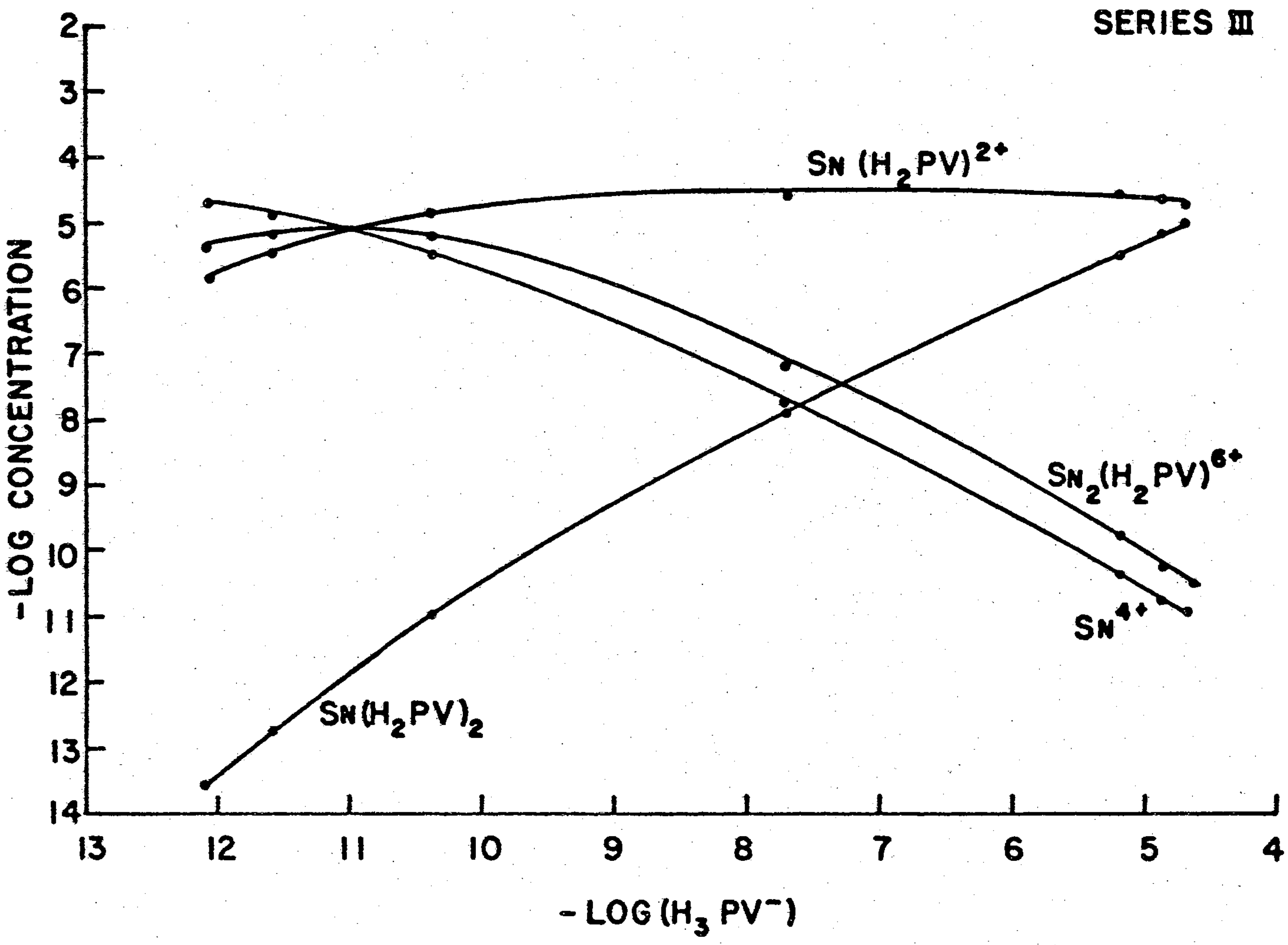


Figure 34. Concentration of Species, Series III

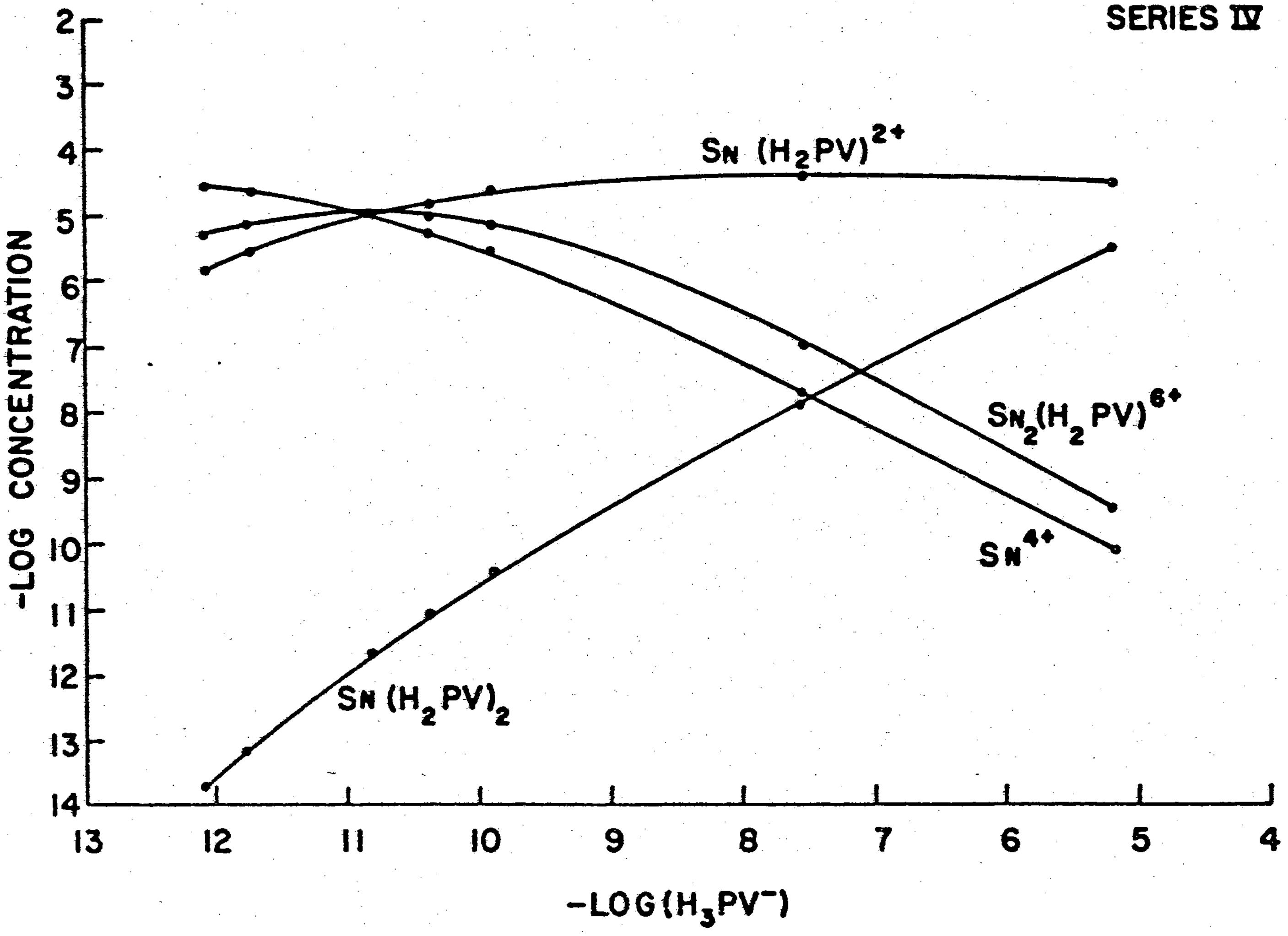


Figure 35. Concentration of Species, Series IV

CHAPTER IX

SUMMARY

An objective computer method for determining the number, nature, and stabilities of complexes in solution from spectrophotometric data has been developed. Six computer programs have been collected, modified, or written and used to interpret absorbance data. These programs constitute a powerful method for analyzing spectrophotometric data from systems containing mononuclear, polynuclear, or a mixture of mononuclear and polynuclear complexes.

Three acid dissociation constants of pyrocatechol violet in 1M Cl^- solutions have been determined:

$$pK_1 = 0.264 \pm 0.003$$

$$pK_2 = 7.508 \pm 0.001$$

$$pK_3 = 8.332 \pm 0.003 .$$

Molar extinction coefficients and concentrations of pyrocatechol violet species were also calculated.

Spectrophotometric data from 1M Cl^- solutions of tin(IV) and pyrocatechol violet have been interpreted on the basis of formation of 1:1, 1:2, and 2:1 metal-ligand complexes. The corresponding stability constants were:

$$\log \beta_{11} = 7.801 \pm 0.133$$

$$\log \beta_{12} = 14.899 \pm 0.297$$

$$\log \beta_{21} = 12.922 \pm 0.342 \quad .$$

Molar extinction coefficients and concentrations of tin(IV) species were calculated.

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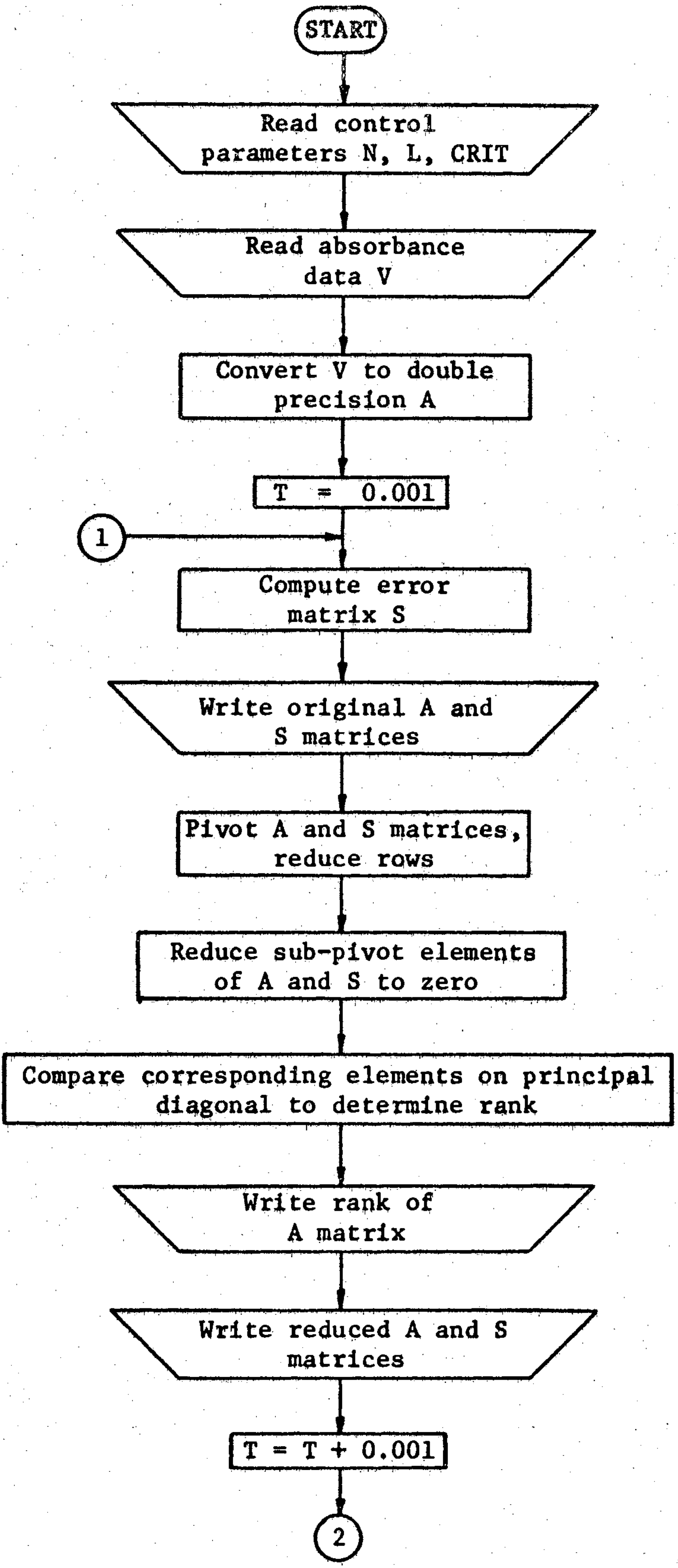
APPENDIX A

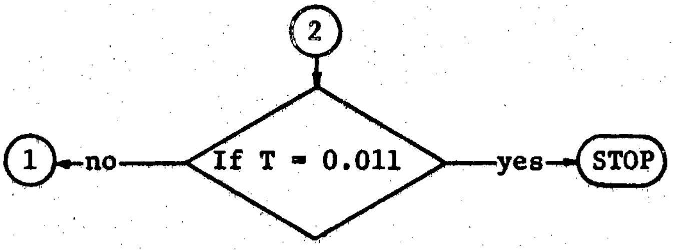
FLOW CHART, PROGRAM LISTING, AND DATA SET FOR MATRIX RANK ANALYSIS

TABLE XX

INPUT REQUIREMENTS FOR MATRIX RANK CALCULATION

Card Number	Columns	Format	Variable Name and Function
1	1-5	I5	N - number of solutions
	6-10	I5	L - number of wavelengths
	11-19	F9.8	CRIT - criterion for setting elements of A to zero
Next M cards	1-80	16(F4.3,1X)	V - absorbance data with number of cards determined by N and L. Solution 1 data starts on card 2 and continues as needed 16 wavelengths per card. Start solution 2 data on another card regardless of where solution 1 data ended on the previous card


START
Read control parameters N, L, CRIT
Read absorbance data V
Convert V to double precision A
T = 0.001
1
Compute error matrix S
Write original A and S matrices
Pivot A and S matrices, reduce rows
Reduce sub-pivot elements of A and S to zero
Compare corresponding elements on principal diagonal to determine rank
Write rank of A matrix
Write reduced A and S matrices
T = T + 0.001
2


2
1
no
If T = 0.011
yes
STOP

```
C      ANALYSIS OF SPECTRA           KATZ-WALLACE
C      PROGRAM CONVERTED TO DOUBLE PRECISION AND MODIFIED BY WILLIAM D. WAKLEY,
C      CHEMISTRY DEPARTMENT, OKLAHOMA STATE UNIVERSITY
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(L,N)
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      METHDD - 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, L  COLS. 6-10, 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
       REAL V(91,9)/819*0.0/,W(91,9)/819*0.0/,CK(91)/91*0.0/
       REAL*8 A(91,9)/819*0.0D+00/,S(91,9)/819*0.0D+00/,Z(91,9)/819*0.0D+
      100/,Y(91,9)/819*0.0D+00/,B(91,9)/819*0.0D+00/,AMAX70.0D+00/,TEMP/0
      2.0D+00/,FAC/0.0D+00/,SW/0.0D+00/,X/0.0D+00/,SW1/0.0D+00/
       REAL*8 DABS,DSQRT,DBLE
     1 FORMAT(2I5,F9.8)
     2 FORMAT(16(F4.3,1X))
     3 FORMAT(1H1,10X,17HRANK OF SYSTEM IS,I3,1X,31HWITHIN A RANGE OF PLU
      1S OR MINUS,F15.5,1X,12HSIGMA LIMITS)
     4 FORMAT(1H1,30X,17HORIGINAL A MATRIX//)
     5 FORMAT(1H1,30X,17HORIGINAL S MATRIX//)
     6 FORMAT(1H1,30X,16HREDUCED A MATRIX//)
     7 FORMAT(1H1,30X,16HREDUCED S MATRIX//)
     8 FORMAT(1HJ,9F12.7)
       READ(5,1) N,L,CRIT
C      READ ABSORBANCE DATA
       DO  103  J=1,N
   103 READ(5,2)  (V(I,J), I=1,L)
C      CONVERT ABSORBANCE DATA TO DOUBLE PRECISION AND STORE ORIGINAL DATA IN B
       DD 321  J=1,N
       DD  321  I=1,L
       A(I,J)=DBLE(V(I,J))
       B(I,J)=A(I,J)
   321 CONTINUE
C      PERFORM RANK CALCULATION 10 TIMES VARYING PHOTOMETRIC ERROR FRDM 0.001
C      TD 0.01
       DO 50 KT=1,10
       T=KT
       T=T*0.001
C      CALCULATE ERRDR MATRIX S
       DO 14 I=1,L
       DO 14 J=1,N
       X=A(I,J)
    14 S(I,J)=0.43429*T*10.**X
       WRITE(6,4)
```

```
C      WRITE ABSORBANCE MATRIX A
       DO  20  I=1,L
    20 WRITE(6,8) (A(I,J), J=1,N)
       WRITE(6,5)
C      WRITE ERROR MATRIX S
       DO  30  I=1,L
    30 WRITE(6,8) (S(I,J), J=1,N)
C
C      MATRIX ELEMENTS READ, NOW TO PIVOT AND REDUCE ROWS
C
       NMIN=N-1
       DO  140  JC=1,NMIN
       AMAX=0.0D+00
       DO  110  I=JC,L
       DO  110  J=JC,N
       IF(AMAX-DABS(A(I,J)).GE.0.)  GO TO 110
   105 AMAX=DABS(A(I,J))
       IMAX=I
       JMAX=J
   110 CONTINUE
       IF(AMAX.LE.0.)  GO TO 150
   112 DO  115  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
       DO  120  I=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
C
       IPLUS=JC+1
       DD  130  I=IPLUS,L
       IF(A(I,JC).EQ.0.)  GO TO 130
   125 FAC=A(I,JC)/A(JC,JC)
       DO  129  J=IPLUS,N
       A(I,J)=A(I,J)-FAC*A(JC,J)
       TEMP=A(JC,J)/A(JC,JC)
       S(I,J)=DSQRT(S(I,J)**2+(S(I,JC)*TEMP)**2+(S(JC,J)*FAC)**2+(S(JC,JC
      1)*FAC*TEMP)**2)
       IF(DABS(A(I,J))-DABS(CRIT*S(I,J)).GT.0.)  GO TO 129
       S(I,J)=0.0D+00
   127 A(I,J)=0.0D+00
   129 CONTINUE
       A(I,JC)=0.0D+00
       S(I,JC)=0.0D+00
   130 CONTINUE
   140 CONTINUE
```

```
      NN=N+1
      SW=A(N,N)
      DO 111 I=NN,L
      IF(DABS(A(I,N)).LE.DABS(SW))   GO TO 1111
      SW=A(I,N)
      SW1=S(I,N)
 1111 A(I,N)=0.0D+00
      S(1,N)=0.0D+00
  111 CONTINUE
      A(N,N)=SW
      S(N,N)=SW1
      IF(A(N,N).NE.0.)  GO TO 150
  142 IF(L-N.LE.0)  GO TO 150
  143 NPLUS=N+1
      DO  145  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(1,N)=SW
      GO TO 150
  145 CONTINUE
C
C     MATRIX IS REDUCED, DETERMINE RANK
C
  150 DO  160  I=1,N
      NRANK=N+1-I
      IF(DABS(A(NRANK,NRANK)).GE.3.*S(NRANK,NRANK))  GO TO 162
  160 CONTINUE
C
C     WRITE RANK REDUCED A AND S MATRICES
C
  162 WRITE(6,3) NRANK,CRIT
      WRITE(6,6)
      DO  165  I=1,L
  165 WRITE(6,8) (A(I,J), J=1,N)
      WRITE(6,7)
      DO  170  I=1,L
  170 WRITE(6,8) (S(I,J), J=1,N)
      DO  171  I=1,L
      DO  171  J=1,N
      A(I,J)=B(I,J)
  171 CONTINUE
   50 CONTINUE
      STOP
      END
C
C     DATA
C
    9   890001
0001 0001 0001 0002 0003 0005 0006 0009 0010 0011 0016 0021 0028 0037 0049 0068
0092 0127 0174 0242 0333 0452 0598 0772 0972 1160 1324 1455 1534 1555 1527 1466
1382 1288 1194 1109 1026 0948 0876 0815 0772 0741 0724 0725 0734 0756 0783 0808
0837 0862 0875 0888 0889 0884 0866 0845 0811 0778 0737 0698 0661 0631 0609 0592
0583 0577 0567 0544 0520 0489 0462 0425 0398 0381 0374 0381 0400 0418 0424 0428
0439 0489 0610 0744 0796 0774 0702 0625 0561
0001 0001 0001 0001 0001 0001 0001 0001 0002 0002 0003 0004 0006 0008 0011 0014
0018 0024 0033 0042 0058 0078 0102 0138 0173 0211 0244 0277 0298 0311 0318 0324
0330 0339 0352 0370 0398 0430 0474 0527 0589 0652 0723 0808 0892 0969 1048 1120
1182 1229 1262 1276 1279 1261 1228 1183 1121 1058 0986 0916 0852 0780 0722 0672
0630 0596 0569 0544 0528 0514 0506 0496 0487 0481 0480 0482 0494 0507 0517 0524
0539 0573 0649 0768 0852 0844 0759 0644 0547
0001 0001 0001 0001 0001 0001 0001 0001 0001 0001 0001 0001 0002 0003 0004 0004
0005 0006 0007 0008 0008 0009 0011 0016 0020 0029 0037 0046 0056 0069 0083 0101
0123 0153 0187 0230 0281 0339 0408 0481 0566 0650 0749 0840 0947 1031 1121 1207
1277 1333 1373 1394 1394 1376 1344 1289 1224 1150 1072 0996 0919 0841 0772 0717
0664 0627 0602 0582 0568 0557 0549 0539 0532 0527 0519 0514 0516 0521 0526 0532
0549 0582 0654 0769 0870 0876 0791 0672 0558
0001 0001 0001 0001 0001 0001 0001 0001 0001 0001 0001 0002 0003 0004 0004 0005
0005 0005 0005 0005 0005 0005 0005 0006 0009 0012 0019 0028 0036 0047 0062 0081
0105 0136 0171 0218 0267 0328 0392 0470 0554 0642 0739 0838 0940 1025 1120 1200
1273 1327 1366 1386 1389 1370 1331 1281 1222 1149 1065 0990 0912 0837 0769 0709
0654 0609 0577 0548 0529 0519 0514 0511 0508 0506 0506 0512 0527 0541 0551 0563
0577 0602 0674 0786 0875 0868 0778 0661 0556
0001 0001 0001 0001 0001 0002 0002 0003 0003 0003 0004 0005 0005 0006 0006 0006
0007 0007 0007 0007 0007 0007 0008 0010 0014 0018 0026 0033 0042 0052 0070 0089
0113 0143 0181 0227 0278 0335 0402 0480 0561 0652 0747 0842 0946 1034 1126 1212
1282 1337 1380 1396 1405 1381 1346 1292 1228 1154 1077 0991 0916 0840 0772 0717
0668 0630 0603 0585 0569 0558 0552 0547 0538 0529 0521 0518 0518 0521 0527 0531
0547 0578 0651 0770 0869 0871 0786 0670 0560
0001 0008 0019 0029 0042 0055 0068 0078 0081 0083 0082 0081 0080 0080 0080 0080
0083 0089 0092 0097 0100 0103 0107 0108 0109 0108 0108 0107 0108 0112 0120 0132
0152 0174 0208 0244 0292 0348 0411 0479 0559 0647 0734 0824 0923 1012 1096 1178
1241 1292 1328 1355 1360 1350 1324 1286 1227 1155 1081 0996 0922 0847 0773 0707
0651 0608 0575 0546 0524 0509 0502 0495 0491 0487 0481 0476 0470 0471 0476 0490
0514 0557 0640 0763 0862 0862 0773 0656 0547
0001 0010 0025 0042 0058 0076 0092 0103 0108 0111 0109 0108 0106 0107 0112 0116
0130 0144 0158 0168 0170 0171 0169 0164 0161 0157 0152 0150 0149 0151 0156 0165
0181 0201 0230 0264 0308 0360 0420 0488 0568 0647 0734 0827 0914 1000 1082 1158
1219 1266 1303 1324 1333 1319 1297 1256 1200 1128 1053 0980 0900 0827 0753 0702
0643 0598 0566 0538 0517 0505 0496 0487 0480 0476 0468 0463 0460 0463 0472 0485
0516 0556 0641 0760 0850 0838 0752 0638 0534
0001 0014 0030 0046 0068 0089 0107 0122 0136 0150 0164 0183 0217 0263 0330 0423
0543 0677 0800 0900 0954 0964 0942 0903 0858 0813 0776 0740 0708 0674 0644 0617
0592 0570 0558 0552 0556 0568 0586 0608 0642 0674 0715 0756 0804 0848 0887 0928
0959 0987 0998 1008 1011 1008 0998 0974 0947 0902 0854 0798 0752 0704 0657 0618
0580 0552 0527 0508 0488 0475 0466 0453 0446 0440 0442 0452 0474 0511 0557 0606
0648 0678 0708 0758 0788 0750 0664 0556 0491
0001 0014 0031 0050 0074 0100 0128 0153 0174 0202 0234 0282 0356 0454 0600 0800
1040 1320 1574 1780 1913 1960 1931 1853 1774 1680 1617 1547 1478 1414 1342 1267
1189 1113 1046 0980 0927 0874 0832 0790 0750 0713 0686 0657 0636 0611 0596 0577
0560 0548 0536 0531 0531 0534 0546 0551 0554 0554 0548 0542 0536 0530 0523 0516
0512 0508 0502 0492 0482 0472 0458 0443 0431 0431 0442 0468 0518 0603 0701 0794
0856 0864 0828 0773 0710 0632 0553 0496 0472
```

APPENDIX B

FLOW CHART, PROGRAM LISTING, AND DATA SET FOR SPECIES NUMBER PROGRAM

TABLE XXI

INPUT REQUIREMENTS FOR SPECIES NUMBER PROGRAM

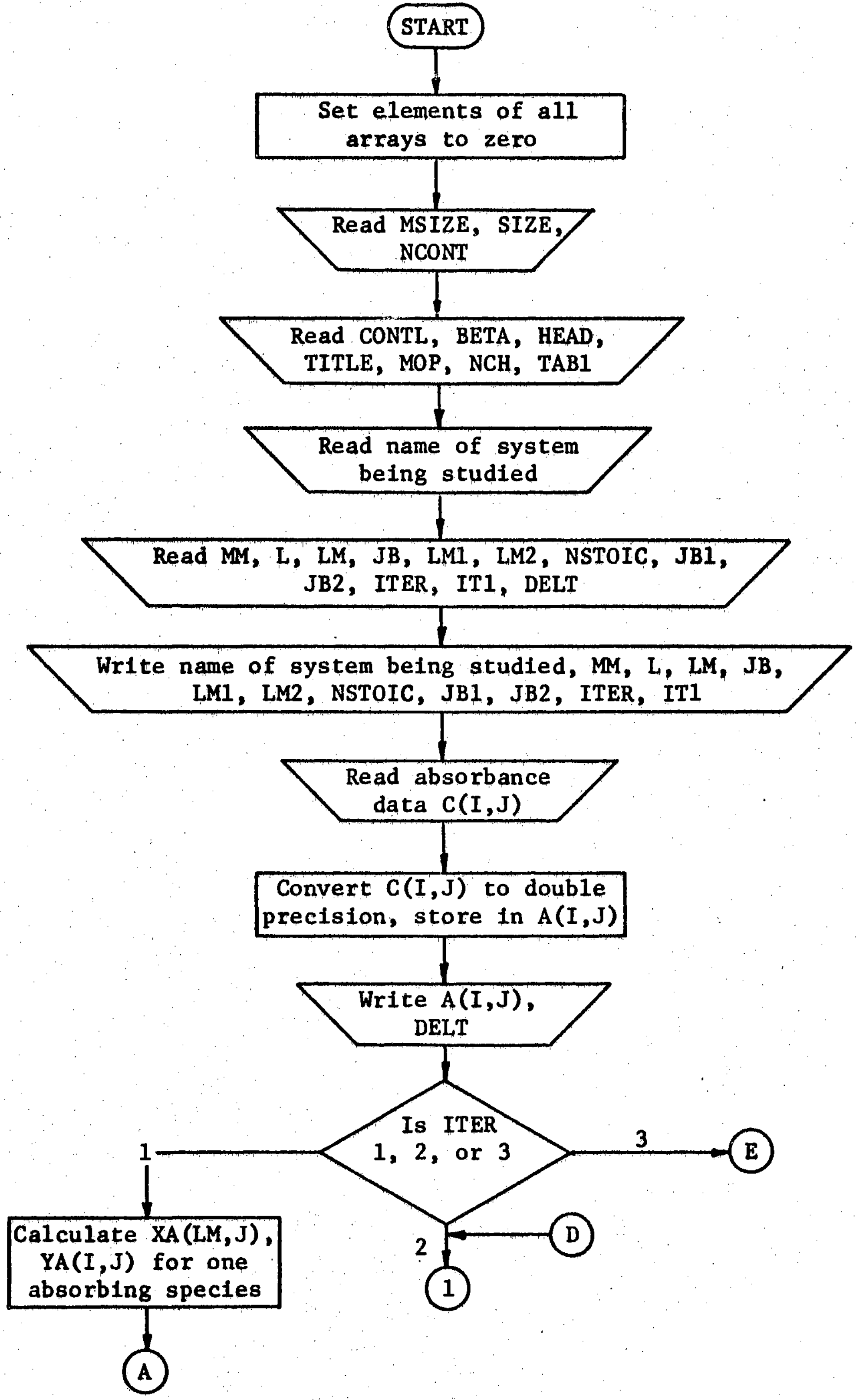
Card Number	Columns	Format	Variable Name and Function
1	1-3	I3	MSIZE - maximum size polynomial for least squares curve fit
	4-6	I3	SIZE - size of polynomial used
	7-9	I3	NCONT - number of polynomials to be tried
2	1-2	I2	CONTL - code for 1st term
	3-4	I2	- code for 2nd term
	5-6	I2	- code for 3rd term
	7-8	I2	- code for 4th term
	9-10	I2	- code for 5th term
	11-12	I2	- code for 6th term
	13-14	I2	- code for 7th term
	15-16	I2	- code for 8th term
			Explanation of code: Terms 1 thru 8 refer to Beta's, coefficients of the polynomial. If 0, this parameter is calculated. If 1, this parameter is not calculated.
3	1-10	D10.3	Beta$_0$
	11-20	D10.3	Beta$_1$
	21-30	D10.3	Beta$_2$
	31-40	D10.3	Beta$_3$
	41-50	D10.3	Beta$_4$

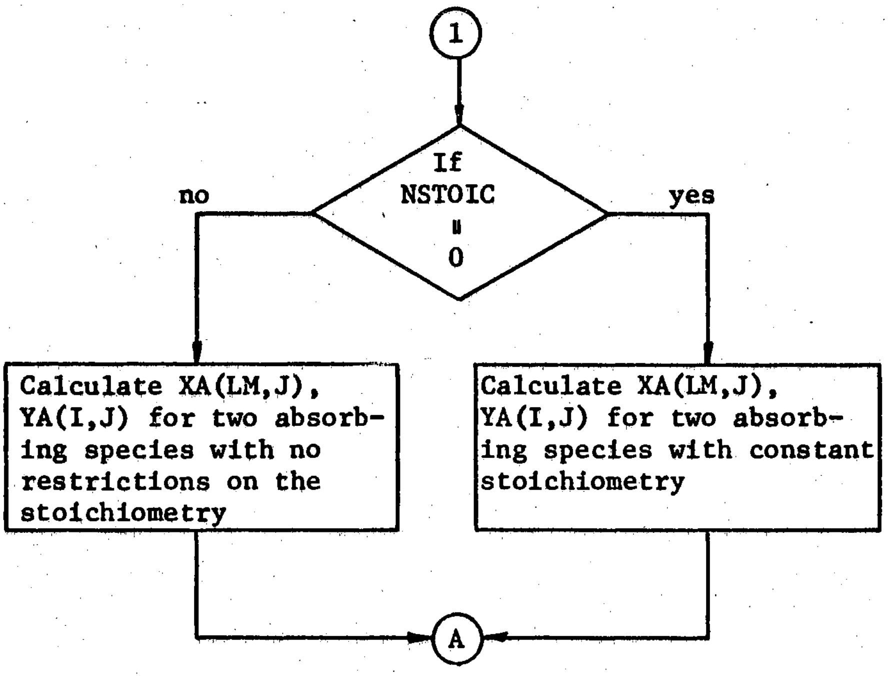
TABLE XXI (Continued)

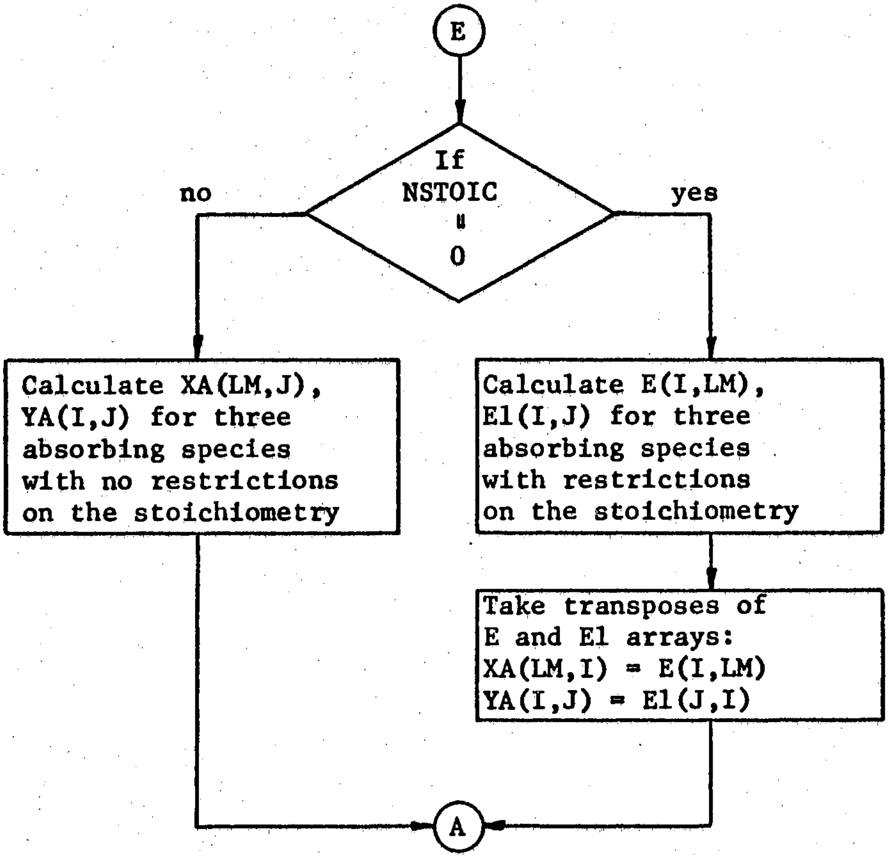
Card Number	Columns	Format	Variable Name and Function
	51-60	D10.3	$Beta_5$
	61-70	D10.3	$Beta_6$
	71-80	D10.3	$Beta_7$
4	1-80	20A4	HEAD - column headings for output table
5	1-80	20A4	TITLE - title for plot
6	1-18	80A1	MOP - title for Y-axis of plot
	19-20		NCH - characters for plotting experimental and calculated data
	59-76		TAB1 - title for X-axis of plot
	77		ND - "."
	78		NP - "+"
	79		NM - "-"
	80		NB - blank
7	1-55	55H	name of the system being studied
8	1-3	I3	MM - number of solution compositions
	4-6	I3	L - number of wavelengths
	7-9	I3	LM - wavelength of maximum absorbance
	10-12	I3	JB - reference solution
	13-15	I3	LM1 - wavelength of maximum absorbance
	16-18	I3	LM2 - wavelength of maximum absorbance

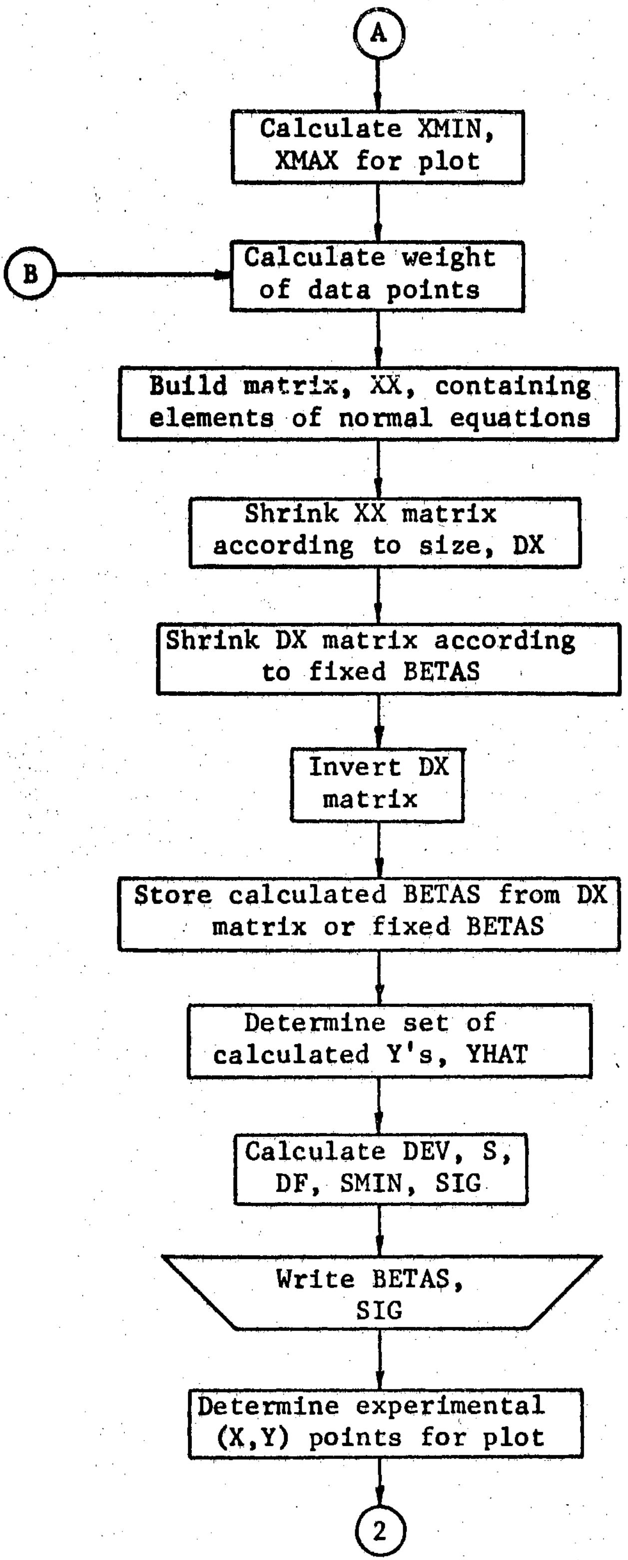
TABLE XXI (Continued)

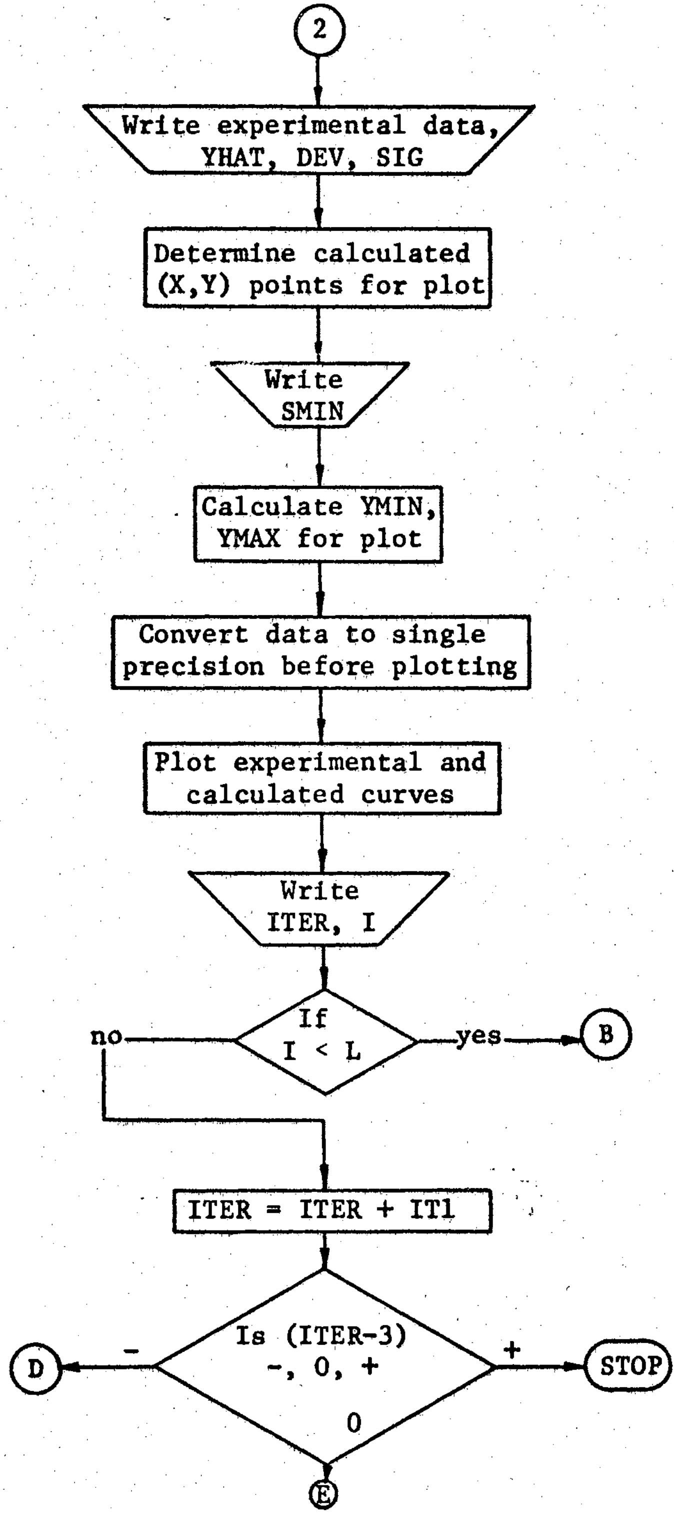
Card Number	Columns	Format	Variable Name and Function
	19-21	I3	NSTOIC - 1 for nonconstant stoichiometry, 0 for constant stoichiometry
	22-24	I3	JB1 - reference solution
	25-27	I3	JB2 - reference solution
	28-30	I3	ITER - iteration number
	31-33	I3	IT1 - control parameter
9	1-10	D10.3	DELT - error parameter used in weight calculation
Next M cards	1-80	16(F4.3,1X)	C - absorbance data with number of cards determined by MM and L. See Table XX for explanation of format


START
Set elements of all arrays to zero
Read MSIZE, SIZE, NCONT
Read CONTL, BETA, HEAD, TITLE, MOP, NCH, TAB1
Read name of system being studied
Read MM, L, LM, JB, LM1, LM2, NSTOIC, JB1, JB2, ITER, IT1, DELT
Write name of system being studied, MM, L, LM, JB, LM1, LM2, NSTOIC, JB1, JB2, ITER, IT1
Read absorbance data C(I,J)
Convert C(I,J) to double precision, store in A(I,J)
Write A(I,J), DELT
Is ITER 1, 2, or 3
1
3
E
2
D
1
Calculate XA(LM,J), YA(I,J) for one absorbing species
A


1
If NSTOIC = 0
no
yes
Calculate XA(LM,J), YA(I,J) for two absorbing species with no restrictions on the stoichiometry
Calculate XA(LM,J), YA(I,J) for two absorbing species with constant stoichiometry
A


E
If NSTOIC = 0
no
yes
Calculate XA(LM,J), YA(I,J) for three absorbing species with no restrictions on the stoichiometry
Calculate E(I,LM), E1(I,J) for three absorbing species with restrictions on the stoichiometry
Take transposes of E and E1 arrays: XA(LM,I) = E(I,LM) YA(I,J) = E1(J,I)
A


A
Calculate XMIN, XMAX for plot
B
Calculate weight of data points
Build matrix, XX, containing elements of normal equations
Shrink XX matrix according to size, DX
Shrink DX matrix according to fixed BETAS
Invert DX matrix
Store calculated BETAS from DX matrix or fixed BETAS
Determine set of calculated Y's, YHAT
Calculate DEV, S, DF, SMIN, SIG
Write BETAS, SIG
Determine experimental (X,Y) points for plot
2


2
Write experimental data, YHAT, DEV, SIG
Determine calculated (X,Y) points for plot
Write SMIN
Calculate YMIN, YMAX for plot
Convert data to single precision before plotting
Plot experimental and calculated curves
Write ITER, I
If I < L
no
yes
B
ITER = ITER + IT1
Is (ITER-3) -, 0, +
-
D
+
STOP
0
E

```
C     L. P. VARGA AND WILLIAM D. WAKLEY  OKLAHOMA STATE UNIVERSITY  CHEMISTRY
C     OEPARTMENT  NUMBER OF ABSORBING SPECIES PROGRAM  FORTRAN IV
C     IBM SYSTEM 360  OSU COMPUTER CENTER  21 NOVEMBER 1968
C     CALCULATES THE (X,Y) FUNCTIONS FOR 1,2,OR 3 ABSORBING SPECIES WITH
C     CONSTANT OR NONCONSTANT STOICHIOMETRY, FITS THE BEST STRAIGHT LINE
C     THRU EACH DATA SET, CALCULATES THE INTERCEPT AND SLOPE OF EACH LINE,
C     CALCULATES THE GOODNESS OF FIT PARAMETER, AND PLOTS THE EXPERIMENTAL
C     AND CALCULATED LINES FOR EACH CASE
      INTEGER CONTL,SIZE
      DOUBLE PRECISION  XX(8,9),DX(8,9),V(11,80),BETA(8),B(8),SIG(8),A(8
     10,10),SA(80,10),XA(80,80),YA(80,80),E(80,1),E1(80,10),YHAT(80),DEV
     2(80),S(80),X(160),Y(160)
      DIMENSION HEAD(20),MOP(18),NCH(41),TITLE(20),TAB1(18),Z(1),CONTL(3
     1,8),C(80,10) ,XS(160),YS(160),CK(80)
      REAL*8 OBLE,DABS,DSQRT
      DOUBLE PRECISION X1,XMIN,XMAX,VARY,YMIN,YMAX,W,PIVOT,AY,SMIN,AYI
      COMMON TITLE,MOP,NCH,TAB1,ND,NP,NM,NB,JREAD5,JRITE6
    1 FORMAT(16(F4.3,1X))
    2 FORMAT(1P7D11.3)
    3 FORMAT(8I2)
    4 FORMAT(12I3)
    5 FORMAT(1X,20A4)
    6 FORMAT(20A4)
    7 FORMAT(55H
    8 FORMAT(88X,12HSMIN/(DF-1)=,D16.6)
   33 FORMAT(8010.3)
   34 FORMAT(1H ,10013.6)
   35 FORMAT(1P2D15.6/)
   36 FORMAT(1H1,6X,4HBETA,10X,7HSTD DEV)
   37 FORMAT(1H2,10X,20H PHOTOMETRIC ERROR =,D16.6
   52 FORMAT(80A1)
      JREAD5=5
      JRITE6=6
C     SET ELEMENTS OF ALL ARRAYS TO ZERO
      DO  60 I=1,80
      DO  60 J=1,80
      XA(I,J)=0.00+00
      YA(I,J)=0.0D+00
   60 CONTINUE
      DO  61 I=1,80
      DO  61 J=1,10
      A(I,J)=0.0D+00
      SA(I,J)=0.0D+00
      E1(I,J)=0.0D+00
   61 CONTINUE
      DO  62 I=1,80
      YHAT(I)=0.0D+00
      DEV(I)=0.0D+00
      S(I)=0.0D+00
   62 CONTINUE
      DO  63 I=1,160
      X(I)=0.0D+00
      Y(I)=0.0D+00
   63 CONTINUE
      DO  64 I=1,11
      DO  64 J=1,80
      V(I,J)=0.0D+00
   64 CONTINUE
      DO  65 I=1,80
      J=1
      E(I,J)=0.0D+00
   65 CONTINUE
      DO  66 I=1,8
      DO  66 J=1,9
      XX(I,J)=0.0D+00
      DX(I,J)=0.0D+00
   66 CONTINUE
      DO  67 I=1,8
      BETA(I)=0.0D+00
      B(I)=0.0D+00
      SIG(I)=0.00+00
   67 CONTINUE
C     MSIZE=MAXIMUM SIZE OF POLYNOMIAL FOR LEAST SQUARES FIT, SIZE=SIZE
C     OF POLYNOMIAL USED, NCONT=NUMBER OF POLYNOMIALS, CONTL=DETERMINES BETAS
C     TO BE FIXED OR CALCULATED, BETA=CONSTANTS IN POLYNOMIAL, HEAD=OUTPUT
C     TABLE HEADINGS, TITLE=TITLE OF PLOT, MOP=ORDINATE OF PLOT, NCH=SYMBOLS
C     USED FOR PLOT, TAB1=ABSCISSA OF PLOT, ND,NP,NM,NB=CONTROL PARAMETERS
C     FOR PLOT, DELT=ERROR PARAMETER, MM=NUMBER OF SOLUTION COMPOSITIONS,
C     L=NUMBER OF WAVELENGTHS, LM1,LM2,LM=WAVELENGTHS OF MAXIMUM ABSORBANCE,
C     JB1,JB2,JB=REFERENCE SOLUTIONS
      READ(JREAD5,4) MSIZE,SIZE,NCONT
      DO 101 K=1,NCONT
  101 READ(JREAD5,3) (CONTL(K,I), I=1,MSIZE)
      READ(JREAD5,33) (BETA(I), I=1,MSIZE)
      READ(JREAD5,6) (HEAD(I), I=1,20)
      READ(JREAD5,6) (TITLE(I), I=1,20)
      READ(JREAD5,52) (MOP(I), I=1,18),(NCH(I), I=1,40),(TAB1(I), I=1,18
     1),ND,NP,NM,NB
 1000 READ(JREAD5,7)
C     THE NAME OF THE SYSTEM BEING STUDIEO IS READ IN HERE.
      READ(JREAD5,4) MM,L,LM,JB,LM1,LM2,NSTOIC,JB1,JB2,ITER,IT1
C     NSTOIC=1 IF NON-CONSTANT STOICHIOMETRY IS ASSUMED, 0 IF CONSTANT
      READ(JREAD5,33) OELT
      WRITE(JRITE6,7)
      WRITE(JRITE6,4) MM,L,LM,JB,LM1,LM2,NSTOIC,JB1,JB2,ITER,IT1
      MS1=MSIZE+1
C     READ ABSORBANCE DATA
      DO 103  J=1,MM
  103 READ(JREAD5,1) (C(I,J),  I=1,L)
C     CONVERT ABSORBANCE DATA TO DOUBLE PRECISION
      DO  53  J=1,MM
      DO  53  I=1,L
      A(I,J)=DBLE(C(I,J))
   53 CONTINUE
C     WRITE ABSORBANCE DATA
      DO 1033 I=1,L
 1033 WRITE(JRITE6,34) (A(I,J), J=1,MM)
      WRITE(JRITE6,37) DELT
      GO TO(1234,3311,1103),ITER
C     STATEMENTS 1234 THRU 5011 CALCULATE FUNCTIONS TO BE PLOTTED
```

```
C     1 ABSORBING SPECIES
 1234 DO 4400 J=1,MM
      XA(LM,J)=A(LM,J)
      DO 4400 I=1,L
      YA(I,J)=A(I,J)
      X1=A(I,J)
 4400 SA(I,J)=0.43429*DELT*10.**X1
 5002 GO TO 1122
C     2 ABSORBING SPECIES, NON-CONSTANT STOICHIOMETRY
 3311 DO 1003 J=1,MM
      IF(NSTOIC.EQ.0) GO TO 1002
 2006 IF(LM.EQ.1)  GO TO 2002
 2007 LMM1=LM-1
      DO 2001 I=1,LMM1
 2001 YA(I,J)=A(I,J)/A(1,J)
      IF(LM.EQ.L)  GO TO 2004
 2002 LMP1=LM+1
      DO 2003 I=LMP1,L
 2003 YA(I,J)=A(I,J)/A(1,J)
 2004 CONTINUE
 2005 XA(LM,J)=A(LM,J)/A(1,J)
      GO TO 1003
C     2 ABSORBING SPECIES, CONSTANT STOICHIOMETRY
 1002 XA(LM,J)=A(LM,J)-A(LM,JB)
      DO 102 I=1,L
  102 YA(I,J)=A(I,J)-A(I,JB)
 1003 CONTINUE
      GO TO 1122
C     3 ABSORBING SPECIES, CONSTANT STOICHIOMETRY
 1103 DO 1202 J=1,MM
      IF(NSTOIC.EQ.1)  GO TO 5000
 5005 IF(J.EQ.JB)  GO TO 1120
 1121 XA(LM,J)=(A(LM2,J)-A(LM2,JB))/(A(LM1,J)-A(LM1,JB))
      GO TO 1211
 1120 XA(LM,J)=0.0D+00
 1211 DO 1202 I=1,L
      IF(J.EQ.JB)  GO TO 1130
 1102 YA(I,J)=(A(I,J)-A(I,JB))/(A(LM1,J)-A(LM1,JB))
      GO TO 1222
 1130 YA(I,J)=0.0D+00
 1222 CONTINUE
 1202 CONTINUE
      GO TO 1122
C     3 ABSORBING SPECIES, NON-CONSTANT STOICHIOMETRY
 5000 L=L-1
      DO 5001 I=1,L
      IF(JB1.EQ.MN)  GO TO 5007
 5006 IF(LM1.EQ.1)  GO TO 5007
      E(I,LM)=(A(LM1,JB1)*A(I,JB2)-A(LM1,JB2)*A(I,JB1))/(A(LM1,JB1)*A(I,
     1MM)-A(LM1,MM)*A(I,JB1))
      GO TO 5008
 5007 E(I,LM)=0.0D+00
 5008 DO 5001 J=1,MM
      IF(JB1.EQ.MM)  GO TO 5009
 5012 IF(LM1.EQ.I)  GO TO 5009
      E1(I,J)=(A(LM1,JB1)*A(I,J)-A(LM1,J)*A(I,JB1))/(A(LM1,JB1)*A(I,MM)-
     1A(LM1,MM)*A(I,JB1))
      GO TO 5001
 5009 E1(I,J)=0.0D+00
 5001 CONTINUE
      DO 5010 I=1,L
      XA(LM,I)=E(I,LM)
 5010 CONTINUE
      DO 5011 I=1,MM
      DO 5011 J=1,L
      YA(I,J)=E1(J,I)
 5011 CONTINUE
      NC1=MM
      MM=L
      L=NC1
C     CALCULATE XMIN,XMAX FOR PLOTS
 1122 XMIN=XA(LM,1)
      DO 199 J=2,MM
      IF(XMIN.LT.XA(LM,J))  GO TO 199
   39 XMIN=XA(LM,J)
  199 CONTINUE
      XMAX=XA(LM,1)
      DO 99 J=2,MM
      IF(XMAX.GT.XA(LM,J))  GO TO 99
   38 XMAX=XA(LM,J)
   99 CONTINUE
      XMAX=XMAX+0.2*(XMAX-XMIN)
C     LEAST SQUARES CALCULATION THRU STATEMENT 100
      DO 100 I=1,L
      DO 10 K=1,MSIZE
      DO 10 J=1,MS1
   10 XX(K,J)=0.0D+00
C     CALCULATE WEIGHT OF DATA POINTS
      DO 12 J=1,MM
      IF(ITER-2) 1133,2222,2211
 1133 VARY=SA(I,J)*SA(I,J)
      GO TO 4401
 2222 IF(NSTOIC.EQ.1)  GO TO 3113
 3333 VARY= SA(I,J)*SA(I,J)+SA(I,JB)*SA(I,JB)
 4401 W=1.0D+00/VARY
      V(MSIZE+3,J)=DSQRT(DABS(VARY))
      GO TO 1111
 2211 IF(J.EQ.JB) GO TO 1112
 3113 W=1.0D+00
      GO TO 2111
 1112 W=0.0D+00
 2111 V(MSIZE+3,J)=W
 1111 V(1,J)=1.0D+00
   29 V(2,J)=XA(LM,J)
      DO 9 II=3,MSIZE
    9 V(II,J)=V(II-1,J)*XA(LM,J)
   27 V(MSIZE+1,J)=YA(I,J)
      V(MSIZE+2,J)=W
C     BUILD MATRIX CONTAINING ELEMENTS OF NORMAL EQUATIONS
      DO 12 II=1,MSIZE
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```
      PIVOT=V(II,J)
      DO 12 JA=1,MS1
   12 XX(II,JA)=XX(II,JA)+W*PIVOT*V(JA,J)
      LL=1
   13 IF(LL.GT.NCONT)  GO TO 25
 1313 LL=LL+1
C     SHRINK MATRIX ACCORDING TO SIZE
      II=1
      DO 16 K=1,SIZE
      JJ=1
      DO I5 J=1,SIZE
      IF(CONTL(LL-1,K).EQ.1)  GO TO 16
 1314 IF(CONTL(LL-1,J).EQ.1)  GO TO 15
 1315 DX(II,JJ)=XX(K,J)
      JJ=JJ+1
   15 CONTINUE
      II=II+1
   16 CONTINUE
C     SHRINK MATRIX ACCORDING TO FIXED BETA
      N=II-1
      M=II
      II=1
      DO 17 K=1,SIZE
      IF(CONTL(LL-1,K).EQ.1)  GO TO 17
 1717 AY=0.0D+00
      DO 22 J=1,SIZE
   22 AY=AY+BETA(J)*XX(K,J)
      DX(II,M)=XX(K,MS1)-AY
      II=II+I
   17 CONTINUE
C     INVERT MATRIX
   18 CALL INVERT(N,M,DX)
      KK=1
      DO 185 K=1,SIZE
      IF(CONTL(LL-1,K).EQ.1)  GO TO 184
C     STORE CALCULATED BETA FROM MATRIX OR FIXED BETA
 1844 B(K)=DX(KK,M)
      KK=KK+1
      GO TO 185
  184 B(K)=BETA(K)
  185 CONTINUE
      SMIN=0.0D+00
C     DETERMINE SET OF CALCULATED BETAS
      DO 21 J=1,MM
      AY=0.0D+00
      DO 32 K=1,SIZE
   32 AY=AY+B(K)*V(K,J)
      YHAT(J)=AY
C     CALCULATE DEVIATION
      DEV(J)=V(MS1,J)-YHAT(J)
C     CALCULATE WEIGHTED SQUARE OF DEVIATION
      S(J)=V(MSIZE+2,J)*DEV(J)*DEV(J)
   21 SMIN=SMIN+S(J)
C     CALCULATE DEGREES OF FREEDOM
      DF=MM-N
```

```
C     CALCULATE GOODNESS-OF-FIT PARAMETER
      SMIN=SMIN/(DF-1.0)
      KK=I
C     CALCULATE STANDARD DEVIATION OF BETAS
      DO 188 K=1,SIZE
      IF(CONTL(LL-1,K).EQ.1)  GO TO 187
 1877 AY1=DX(KK,KK)*SMIN
      AY=DABS(AY1)
      SIG(K)=DSQRT(AY)
 3131 KK=KK+1
      GO TO 188
  187 SIG(K)=0.0D+00
  188 CONTINUE
 3434 WRITE(JRITE6,36)
C     WRITE BETAS AND STANDARD DEVIATIONS
      WRITE(JRITE6,35) (B(K),SIG(K),K=1,SIZE)
C     WRITE OUTPUT TABLE HEADINGS
      WRITE(JRITE6,5) (HEAD(K), K=1,20)
      DO 23 K=1,MM
      X(K)=V(2,K)
      Y(K)=V(MS1,K)
C     WRITE 3 COLUMNS OF INPUT DATA, WEIGHT, Y CALCULATED, DEVIATION,
C     WEIGHTED SUM OF SQUARES OF DEVIATION
   23 WRITE(JRITE6,2) V(2,K),V(MS1,K),V(MSIZE+3,K),V(MSIZE+2,K),YHAT(K),
     1DEV(K),S(K)
      DO 24 K=1,MM
      J=K+MM
      Y(J)=YHAT(K)
   24 X(J)=V(2,K)
      WRITE(JRITE6,8) SMIN
      Z(I)=1.0
      YMIN=Y(1)
      NPTS=MM+MM
C     CALCULATE YMAX, YMIN FOR PLOT
      DO 399 J=2,NPTS
      IF(YMIN.LT.Y(J))  GO TO 399
   41 YMIN=Y(J)
  399 CONTINUE
      YMAX=Y(1)
      DO 299 J=2,NPTS
      IF(YMAX.GT.Y(J))  GO TO 299
   40 YMAX=Y(J)
  299 CONTINUE
      YMAX=YMAX+0.1*(YMAX-YMIN)
C     CONVERT (X,Y) POINTS TO SINGLE PRECISION
      DO  55  IJ=1,NPTS
      XS(IJ)=SNGL(X(IJ))
      YS(IJ)=SNGL(Y(IJ))
   55 CONTINUE
      XIN=SNGL(XMIN)
      XAX=SNGL(XMAX)
      YIN=SNGL(YMIN)
      YAX=SNGL(YMAX)
C     PLOT EXPERIMENTAL AND CALCULATED CURVES
  409 CALLPLOT(XS,XIN,XAX,0,YS,YIN,YAX,0,Z,0.0,0.0,0,NPTS,2,1,0,2)
```

```
      WRITE(JRITE6,4)  ITER,I
      GO TO 13
   25 CONTINUE
  100 CONTINUE
      ITER=ITER+IT1
C     GO TO NEXT MODEL OR STOP
      IF(ITER-3)  3311,1103,1001
 1001 CONTINUE
      STOP
      END
      SUBROUTINEPLOT(X,XMIN,XMAX,LX,Y,YMIN,YMAX,LY,Z,ZMIN,ZMAX,LZ,NPT,
     1NPLOT,NCOPY,NCD,NDIM)
C     X,Y,Z=SINGLE SUBSCRIPTED VARIABLES IDENTIFYING THE COORDINATES OF THE
C     POINTS TO BE PLOTTED.  XMIN,XMAX,YMIN,YMAX,ZMIN,ZMAX=MINIMUM AND MAXIMUM
C     VALUES ON THE X,Y,AND Z AXES.  LX,LY,LZ=TYPE OF SCALE USED ON THE X,Y,AND
C     Z AXES.  NPTS=TOTAL NUMBER OF POINTS TO BE PLOTTED.  NDIM=DIMENSIONALITY
C     OF THE FUNCTION TO BE PLOTTED.  NPLOTS=NUMBER OF TWO DIMENSIONAL
C     RELATIONSHIPS TO BE PLOTTED.  NCARDS=NUMBER OF INFORMATION CARDS TO BE
C     READ BY PLOT SUBROUTINE
      DIMENSION X(1),Y(1),Z(1),SX(13),TITLE(20),L(134),NCH(41),MOP(18),
     1TAB1(18)
      COMMON TITLE,MOP,NCH,TAB1,ND,NP,NM,NB,JREAD5,JRITE6
    1 FORMAT(20A4)
    2 FORMAT(80A1)
    3 FORMAT(1H1,26X,20A4)
    4 FORMAT(1H ,A1,3X,F6.3,121A1)
    5 FORMAT(132A1)
   12 FORMAT(1HK,62X,18A1)
    6 FORMAT(9X,F6.2,11(4X,F6.2))
    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)
      LLX=LX+1
      NDD=NCD+1
      GO TO(15,13,14,13),NDD
   13 READ(JREAD5,1) (TITLE(I), I=1,20)
   14 IF(NDD.GE.3)READ(JREAD5,2) (MOP(I), I=1,18), (NCH(I), I=1,41),
     1(TAB1(I), I=1,18),ND,NP,NM,NB
   15 NCH(41)=NB
      NPN=NPT/NPLOT
      IF(LX.GT.0)  GO TO 17
 1717 CX=120./(XMAX-XMIN)
      SX(1)=XMIN
      SX(13)=XMAX
      U=XMIN
      DO 16 K=2,12
      U=(XMAX-XMIN)/12.+U
   16 SX(K)=U
      GO TO 19
   17 XLX=LX
      CX=120./XLX
      NX=ALOG10(XMIN)
      DO 18 K=1,LLX
   18 SX(K)=10.**(NX+K-1)
   19 CALLPOT(X,XMIN,LX,NPT,0,120.,CX)
      IF(LY.GT.0)  GO TO 20
 2020 CY=50./(YMAX-YMIN)
      GO TO 21
   20 YLY=LY
      CY=50./YLY
      KY=CY
      NY=ALOG10(YMIN)
   21 CALLPOT(Y,YMIN,LY,NPT,1,50.,CY)
      IF(NDIM.LT.3)  GO TO 24
 2424 IF(LZ.GT.0)  GO TO 22
 2222 CZ=40./(ZMAX-ZMIN)
      GO TO 23
   22 ZLZ=LZ
      CZ=40./ZLZ
   23 CALLPOT(Z,ZMIN,LZ,NPT,0,40.,CZ)
   24 DO 50 NN=1,NCOPY
      M1=1
      T1=33.
      LYY=LY
      TT=50.
      WRITE(JRITE6,3) (TITLE(I), I=1,20)
      DO 43 KK=1,51
      N=1
      NNN=NPN
      JED=1
      T=51-KK
      DO 25 J=1,133
   25 L(J)=NB
      L(133)=ND
      IF(LY.GT.0)  GO TO 26
 2626 L(13)=NP
      IF(T.GT.TT)  GO TO 30
 3030 SCALE=T/CY+YMIN
      L(133)=NP
      N=0
      TT=TT-5.
      IF(T.LE.0.) SCALE=YMIN
  303 GO TO 30
   26 GO TO(27,27,28,28,27,28),LY
   27 SS=KY*LYY
      GO TO 29
   28 SS=KY*LYY+1
   29 L(13)=ND
      IF(T.GT.SS)  GO TO 30
 2929 SCALE=10.**(NY+LYY)
      N=0
      LYY=LYY-1
      L(13)=NP
      L(133)=NP
   30 IF(50..EQ.T)  GO TO 31
  313 IF(0..NE.T)  GO TO 37
   31 DO 32 J=14,133
   32 L(J)=NM
```

```
      IF(LX.GT.0)  GO TO 34
  444 DO 33 J=13,133,10
   33 L(J)=NP
      GO TO 36
   34 KX=120/LX
      DO 35 J=13,133,KX
   35 L(J)=NP
   36 IF(50..EQ.T) L(133)=ND
   37 DO 40 LM=1,NPLOT
      DO 39 I=JED,NNN
      IF(Y(I).NE.T)  GO TO 39
 9393 J=X(I)
      IF(NDIM.NE.3)  GO TO 38
 8383 IZ=Z(I)
      L(J+13)=NCH(IZ+1)
      GO TO 39
   38 L(J+13)=NCH(LM)
   39 CONTINUE
      JED=NNN+1
      NNN=NNN+NPN
   40 CONTINUE
      IF(T1.NE.T)  GO TO 41
  411 IF(15..GE.T)  GO TO 41
  412 L(2)=MOP(M1)
      M1=M1+1
      T1=T1-1.
   41 IF(N.EQ.1)  GO TO 42
 2420 WRITE(JRITE6,4) L(2),SCALE,(L(J), J=12,132)
      GO TO 43
   42 WRITE(JRITE6,5) (L(J), J=1,132)
   43 CONTINUE
      GO TO(44,45,46,47,48,49,44),LLX
   44 WRITE(JRITE6,6) (SX(K), K=1,11)
      GO TO 50
   45 WRITE(JRITE6,7) (SX(K), K=1,LLX)
      GO TO 50
   46 WRITE(JRITE6,8) (SX(K), K=1,LLX)
      GO TO 50
   47 WRITE(JRITE6,9) (SX(K), K=1,LLX)
      GO TO 50
   48 WRITE(JRITE6,10) (SX(K), K=1,LLX)
      GO TO 50
   49 WRITE(JRITE6,11) (SX(K), K=1,LLX)
   50 WRITE(JRITE6,12) (TAB1(I), I=1,18)
      RETURN
      END
      SUBROUTINEPOT(V,VMIN,LV,NP,J,VC,C)
      DIMENSION V(1)
      IF(LV.GT.0)  GO TO 2
   22 DO 1 I=1,NP
    1 V(I)=FLOAT(IFIX(C*(V(I)-VMIN)+.5))
      GO TO 4
    2 DO 3 I=1,NP
    3 V(I)=FLOAT(IFIX(C*(ALOG(V(I)/VMIN)/2.302585)+.5))
    4 IF(J.GT.0)  GO TO 7
```

```
   77 DO 6 I=1,NP
      IF(V(I).LT.0.)  GO TO 5
   55 IF(V(I).LE.VC)  GO TO 6
    5 V(I)=VC+1.
    6 CONTINUE
    7 RETURN
      END
      SUBROUTINE INVERT(N,M,DX)
      DOUBLE PRECISION DX,PIVOT1,PIVOT2
      DIMENSION DX(8,9)
      DO 30 I=1,N
      PIVOT1=1.DO/DX(I,I)
      DX(I,I)=PIVOT1
      DO 10 J=1,M
      IF(J.EQ.I)  GO TO 10
 1010 DX(I,J)=PIVOT1*DX(I,J)
   10 CONTINUE
      DO 25 K=1,N
      IF(K.EQ.I)  GO TO 25
 2525 PIVOT2=DX(K,I)
      DX(K,I)=-PIVOT2*PIVOT1
      DO 20 L=1,M
      IF(L.EQ.I)  GO TO 20
 2020 DX(K,L)=DX(K,L)-PIVOT2*DX(I,L)
   20 CONTINUE
   25 CONTINUE
   30 CONTINUE
      RETURN
      END
C
C     DATA
C
  8  2  1
 0 0 1 1 1 1 1 1
 0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00
     X          Y         SIG  Y        W         YHAT        Y-YHAT    W(Y-YHAT)**2
        COLEMANS SPECIES NUMBER ABSORBANCE DATA PLOT
Y ABSORBANCE FUNCTX*                                                 X ABSORBANCE FUNCT.+-
1    PCV-SN COMPLEXES
  7 16  1  1 12  5  1  1  2  3  1
 0.005D+00
0056 0114 0149 0147 0126 0081 D052 0050 0055 0060 0057 0060 0076 0071 0084 0098
0078 0162 0209 0213 0189 0121 0076 0068 0073 0077 0075 0075 0094 0082 0100 0119
0110 0242 0352 0413 0495 0338 0177 0129 0126 0131 0133 0137 0163 0111 0149 0208
0129 0276 0402 0498 0678 0477 0234 0162 0150 0155 0164 0171 0195 0121 0170 0257
0140 0298 0451 0582 0878 0627 0298 0195 0178 0182 0198 0211 0230 0138 0197 0304
0158 0308 0489 0714 1255 0949 0427 0263 0229 0231 0263 0292 0299 0169 0252 0411
0176 D325 0525 0834 1578 1210 0539 0329 0288 0292 0337 0375 0366 0205 0309 0513
```

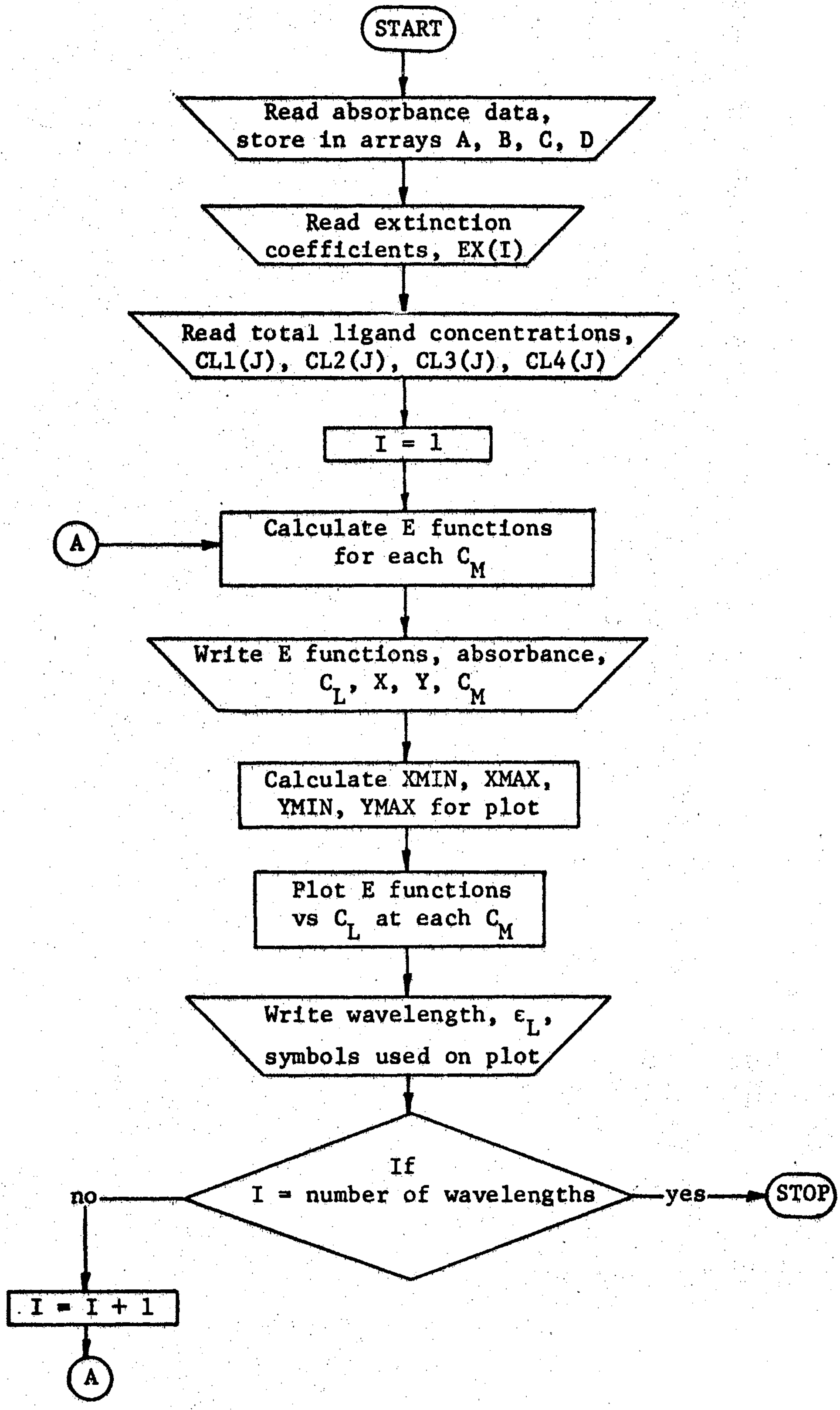
APPENDIX C

FLOW CHART, PROGRAM LISTING, AND DATA SET FOR CORRESPONDING SOLUTIONS PLOT PROGRAM

TABLE XXII

INPUT REQUIREMENTS FOR CORRESPONDING SOLUTIONS PLOT PROGRAM

Card Number	Columns	Format	Variable Name and Function
1	1-80	20A4	TITLE - title for plot
2	1-18	80A1	MOP - title for Y-axis of plot
	19-22		NCH - symbols for plot
	59-76		TAB1 - title for X-axis of plot
	77		ND - "."
	78		NP - "+"
	79		NM - "-"
	80		NB - blank
3	1-3	I3	N - number of solutions
	4-6	I3	M - number of wavelengths
Next MM cards	1-80	16(F4.3,1X)	A, B, C, D - absorbance data with number of cards determined by N and M. See Table XX for explanation of format
Next MM1 cards	1-80	10(F6.1,2X)	EX - molar extinction coefficients of ligand, number of cards determined by M
Next MM2 cards	1-80	7(E10.3)	CL1, CL2, CL3, CL4 - C_L concentrations for each C_M.


START
Read absorbance data, store in arrays A, B, C, D
Read extinction coefficients, EX(I)
Read total ligand concentrations, CL1(J), CL2(J), CL3(J), CL4(J)
I = 1
A
Calculate E functions for each C_M
Write E functions, absorbance, C_L, X, Y, C_M
Calculate XMIN, XMAX, YMIN, YMAX for plot
Plot E functions vs C_L at each C_M
Write wavelength, ϵ_L, symbols used on plot
If I = number of wavelengths
no
yes
STOP
I = I + 1
A

```
C     WILLIAM D. WAKLEY  OKLAHOMA STATE UNIVERSITY  CHEMISTRY DEPARTMENT
C     CORRESPONDING SOLUTIONS PLOT PROGRAM  FORTRAN IV  IBM SYSTEM 360
C     OSU COMPUTER CENTER  14 JULY 1969
C     READS IN ABSORBANCE DATA FOR I WAVELENGTHS AND J EXPERIMENTS, EXTINCTION
C     COEFFICIENTS OF LIGAND AT I WAVELENGTHS, TOTAL LIGAND CONCENTRATION FOR
C     J EXPERIMENTS AT EACH TOTAL METAL CONCENTRATION.  CALCULATES
C     CORRESPONDING SOLUTIONS FUNCTIONS E1,E2,E3,E4.   WRITES EXPERIMENTAL
C     AND CALCULATED DATA.  PLOTS, AT EACH WAVELENGTH, CORRESPONDING
C     SOLUTION FUNCTIONS VS TOTAL LIGAND CONCENTRATION FOR EACH METAL
C     CONCENTRATION.  NUMBER OF CURVES ON EACH PLOT IS EQUAL TO THE NUMBER
C     OF METAL CONCENTRATIONS.  NUMBER OF POINTS ON EACH PLOT IS DETERMINED
C     BY THE NUMBER OF LIGAND CONCENTRATIONS AT EACH METAL CONCENTRATION.
      REAL E1(80,7)/560*0.0/,E2(80,7)/560*0.0/,E3(80,7)/560*0.0/,E4(80,7
     1)/560*0.0/,A(80,7)/560*0.0/,B(80,7)/560*0.0/,C(80,7)/560*0.0/,D(80
     2,7)/560*0.0/,EX(80)/80*0.0/,CM1/1.0E-05/,CM2/2.0E-05/,CM3/3.0E-05/
     3,CM4/4.0E-05/,CL1(7)/7*0.0/,CL2(7)/7*0.0/,CL3(7)/7*0.0/,CL4(7)/7*0
     4.0/,X(28)/28*0.0/,Y(28)/28*0.0/,XMAX/0.0/,XMIN/0.0/,Z(1)/1*0.0/,YM
     5IN/0.0/,YMAX/0.0/,CK(91)/91*0.0/
      DIMENSION MOP(18),NCH(41),TITLE(20),TAB1(18)
    1 FORMAT(16(F4.3,1X))
    6 FORMAT(7E10.3)
    7 FORMAT(10(F6.1,2X))
   13 FORMAT(1P6E16.6)
   14 FORMAT(1H1, 8X,1HE,14X,3HABS,14X,2HCL,14X,1HX,15X,1HY,14X,2HCM)
   23 FORMAT(20A4)
   24 FORMAT(80A1)
   25 FORMAT(I3,3X,11HWAVELENGTH=,I3,3X,10HEXT COEFF=,E16.6)
   27 FORMAT(2I3)
   29 FORMAT(1X,18HCM1 = 1.00E-05 = .)
   30 FORMAT(1X,18HCM2 = 2.00E-05 = *)
   31 FORMAT(1X,18HCM3 = 3.00E-05 = ')
   32 FORMAT(1X,18HCM4 = 4.00E-05 = X)
      COMMON TITLE,MOP,NCH,TAB1,ND,NP,NM,NB,JREAD5,JRITE6
      JREAD5=5
      JRITE6=6
C     READ TITLE OF PLOT
      READ(5,23) (TITLE(I), I=1,20)
C     MOP=ORDINATE OF PLOT  NCH=SYMBOLS FOR PLOT  TAB1=ABSCISSA FOR PLOT
C     ND,NP,NM,NB=CONTROL PARAMETERS FOR PLOT
      READ(5,24) (MOP(I), I=1,18),(NCH(I), I=1,40),(TAB1(I), I=1,18),ND,
     1NP,NM,NB
C     N=NUMBER OF SOLUTIONS  M=NUMBER OF WAVELENGTHS
      READ(5,27) N,M
C     READ ABSORBANCE DATA
      DO 2  J=1,N
    2 READ(5,1) (A(I,J), I=1,M)
      DO 3  J=1,N
    3 READ(5,1) (B(I,J), I=1,M)
      DO 4  J=1,N
    4 READ(5,1) (C(I,J), I=1,M)
      DO 5  J=1,N
    5 READ(5,1) (D(I,J), I=1,M)
C     READ EXTINCTION COEFFICIENTS FOR LIGAND
      READ(5,7) (EX(I), I=1,M)
C     CL1,CL2,CL3,CL4=TOTAL LIGAND CONCENTRATIONS FOR EACH METAL CONCENTRATION
```

```
      READ(5,6) (CL1(J), J=1,N)
      READ(5,6) (CL2(J), J=1,N)
      READ(5,6) (CL3(J), J=1,N)
      READ(5,6) (CL4(J), J=1,N)
C     CALCULATE CORRESPONDING SOLUTION FUNCTIONS
      DO 26  I=1,M
      DO 8  J=1,N
      E1(I,J)=(A(I,J)-EX(I)*CL1(J))/CM1
      E2(I,J)=(B(I,J)-EX(I)*CL2(J))/CM2
      E3(I,J)=(C(I,J)-EX(I)*CL3(J))/CM3
      E4(I,J)=(D(I,J)-EX(I)*CL4(J))/CM4
    8 CONTINUE
      WRITE(6,14)
C     WRITE E FUNCTION, ABSORBANCE, TOTAL LIGAND, X, Y, TOTAL METAL FOR EACH
C     WAVELENGTH
      DO 9  K=1,N
      X(K)=CL1(K)
      Y(K)=E1(I,K)
    9 WRITE(6,13) E1(I,K),A(I,K),CL1(K),X(K),Y(K),CM1
      DO 10  K=1,N
      L=K+N
      X(L)=CL2(K)
      Y(L)=E2(I,K)
   10 WRITE(6,13) E2(I,K),B(I,K),CL2(K),X(L),Y(L),CM2
      DO 11 K=1,N
      L=K+2*N
      X(L)=CL3(K)
      Y(L)=E3(I,K)
   11 WRITE(6,13) E3(I,K),C(I,K),CL3(K),X(L),Y(L),CM3
      DO 12  K=1,N
      L=K+3*N
      X(L)=CL4(K)
      Y(L)=E4(I,K)
   12 WRITE(6,13) E4(I,K),D(I,K),CL4(K),X(L),Y(L),CM4
      NN=4*N
C     SCALE TOTAL LIGAND CONCENTRATIONS BEFORE PLOTTING
      DO 28 L=1,NN
      X(L)=X(L)*10**5.
   28 CONTINUE
C     CALCULATE XMIN,XMAX FOR PLOT
      XMIN=X(1)
      DO 15  L=2,NN
      IF(XMIN.LT.X(L))  GO TO 15
   16 XMIN=X(L)
   15 CONTINUE
      XMAX=X(1)
      DO 17  L=2,NN
      IF(XMAX.GT.X(L))  GO TO 17
   18 XMAX=X(L)
   17 CONTINUE
      XMAX=XMAX+0.2*(XMAX-XMIN)
C     CALCULATE YMIN,YMAX FOR PLOT
      YMIN=Y(1)
      DO 19  L=2,NN
      IF(YMIN.LT.Y(L))  GO TO 19
```

```
   20 YMIN=Y(L)
   19 CONTINUE
      YMAX=Y(1)
      DO 21  L=2,NN
      IF(YMAX.GT.Y(L))  GO TO 21
   22 YMAX=Y(L)
   21 CONTINUE
      YMAX=YMAX+0.1*(YMAX-YMIN)
      Z(1)=1.0
C     PLOT E FUNCTION VS TOTAL LIGAND CONCENTRATION FOR EACH TOTAL METAL
C     CONCENTRATION AT EACH WAVELENGTH
      CALLPLOT(X,XMIN,XMAX,0,Y,YMIN,YMAX,0,Z,0.0,0.0,0,28,4,1,0,2)
      M1=665-I*5
C     WRITE WAVELENGTH, EXTINCTION COEFFICIENTS FOR LIGAND, SYMBOLS USEO
C     ON PLOT FOR EACH TOTAL METAL CONCENTRATION
      WRITE(6,25) I,M1,EX(I)
      WRITE(6,29)
      WRITE(6,30)
      WRITE(6,31)
      WRITE(6,32)
   26 CONTINUE
      STOP
      END
C     SUBROUTINE PLOT AND SUBROUTINE POT ARE THE SAME AS SHOWN IN THE SPECIES
C     NUMBER PROGRAM
C
C     DATA
C
 E VS CL AT CONSTANT CM BY METHOD OF CORRESPONDING SOLUTIONS, PCV-SN SYSTEM
E=(A-EX*CL)/CM     .**X                                     TOTAL LIGANO*10**5.+-
  7 16
0098 0102 0107 0112 0115 0117 0113 0107 0096 0085 0077 0069 0063 0059 0056 0054
0164 0187 0214 0247 0279 0295 0296 0279 0249 0217 0183 0159 0139 0124 0112 0105
0237 0285 0342 0404 0458 0489 0489 0466 0422 0370 0317 0275 0238 0217 0202 0189
0244 0291 0350 0418 0478 0511 0512 0486 0446 0395 0348 0306 0278 0259 0251 0249
0253 0303 0363 0429 0490 0528 0532 0510 0471 0421 0376 0342 0316 0304 0302 0309
0263 0309 0372 0435 0497 0533 0538 0517 0477 0436 0395 0366 0350 0348 0355 0368
0264 0311 0372 0437 0495 0529 0538 0515 0484 0446 0413 0388 0380 0386 0404 0428
0118 0117 0115 0113 0107 0103 0095 0088 0079 0072 0065 0058 0053 0050 0049 0048
0216 0222 0232 0243 0252 0255 0247 0233 0208 0183 0161 0142 0127 0116 0107 0100
0335 0386 0454 0529 0589 0619 0610 0574 0518 0451 0387 0327 0280 0246 0220 0199
0472 0564 0679 0795 0888 0934 0927 0877 0794 0698 0597 0504 0427 0357 0328 0297
0478 0571 0682 0802 0901 0944 0938 0887 0807 0716 0617 0529 0457 0408 0370 0347
0514 0604 0713 0820 0907 0949 0942 0895 0818 0727 0638 0563 0488 0444 0418 0402
0506 0598 0710 0823 0912 0959 0949 0902 0831 0743 0659 0582 0521 0483 0467 0460
0124 0120 0119 0113 0109 0103 0096 0088 0079 0072 0065 0058 0055 0051 0050 0048
0207 0209 0209 0210 0204 0198 0186 0172 0156 0137 0120 0109 0089 0090 0083 0079
0421 0451 0489 0532 0562 0576 0556 0518 0461 0398 0340 0291 0252 0223 0200 0180
0572 0648 0738 0836 0913 0946 0929 0872 0786 0686 0587 0491 0416 0359 0317 0281
0701 0821 0969 1104 1224 1278 1262 1193 1087 0951 0812 0686 0576 0491 0429 0381
0797 0921 1066 1210 1321 1371 1348 1271 1158 1025 0872 0739 0631 0547 0487 0441
0788 0923 1062 1209 1335 1387 1368 1295 1187 1051 0913 0776 0668 0592 0539 0499
0144 0141 0138 0133 0126 0117 0108 0099 0089 0081 0072 0066 0059 0056 0052 0051
0211 0209 0204 0197 0189 0178 0167 0152 0136 0121 0108 0097 0088 0081 0076 0071
0426 0444 0463 0482 0495 0495 0477 0439 0391 0338 0289 0252 0221 0197 0177 0163
```

```
0527 0558 0600 0645 0678 0689 0664 0616 0550 0477 0407 0347 0300 0263 0234 0212
0628 0684 0751 0825 0878 0895 0857 0806 0718 0627 0532 0453 0387 0337 0298 0267
0793 0900 1022 1154 1255 1298 1272 1196 1084 0949 0806 0677 0593 0488 0427 0378
0955 1097 1271 1447 1578 1629 1601 1508 1370 1210 1036 0867 0726 0621 0539 0476
001143  001714  002429  003429  004143  005429  007714  010143  013000  017000
021857  027429  033143  040857  050714  058714
 0.500E-05 0.100E-04 0.200E-04 0.300E-04 0.400E-04 0.500E-04 0.600E-04
 0.500E-05 0.100E-04 0.200E-04 0.300E-04 0.400E-04 0.500E-04 0.600E-04
 0.600E-05 0.100E-04 0.200E-04 0.300E-04 0.400E-04 0.500E-04 0.600E-04
 0.667E-05 0.100E-04 0.200E-04 0.250E-04 0.300E-04 0.400E-04 0.500E-04
```

APPENDIX D

FLOW CHART, PROGRAM LISTING, AND DATA SET FOR CORRESPONDING SOLUTIONS

$\bar{n}$, [L] PROGRAM

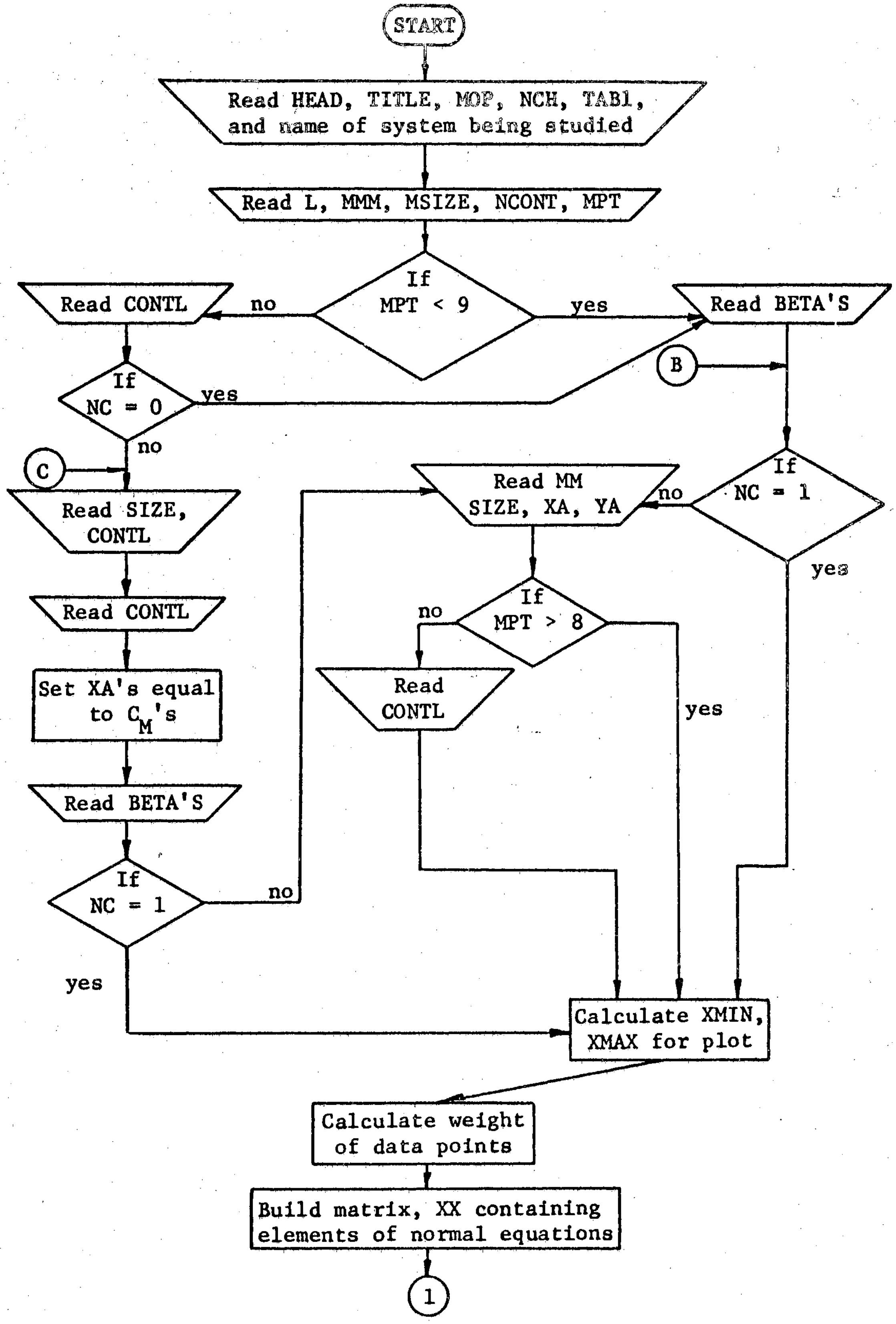
TABLE XXIII

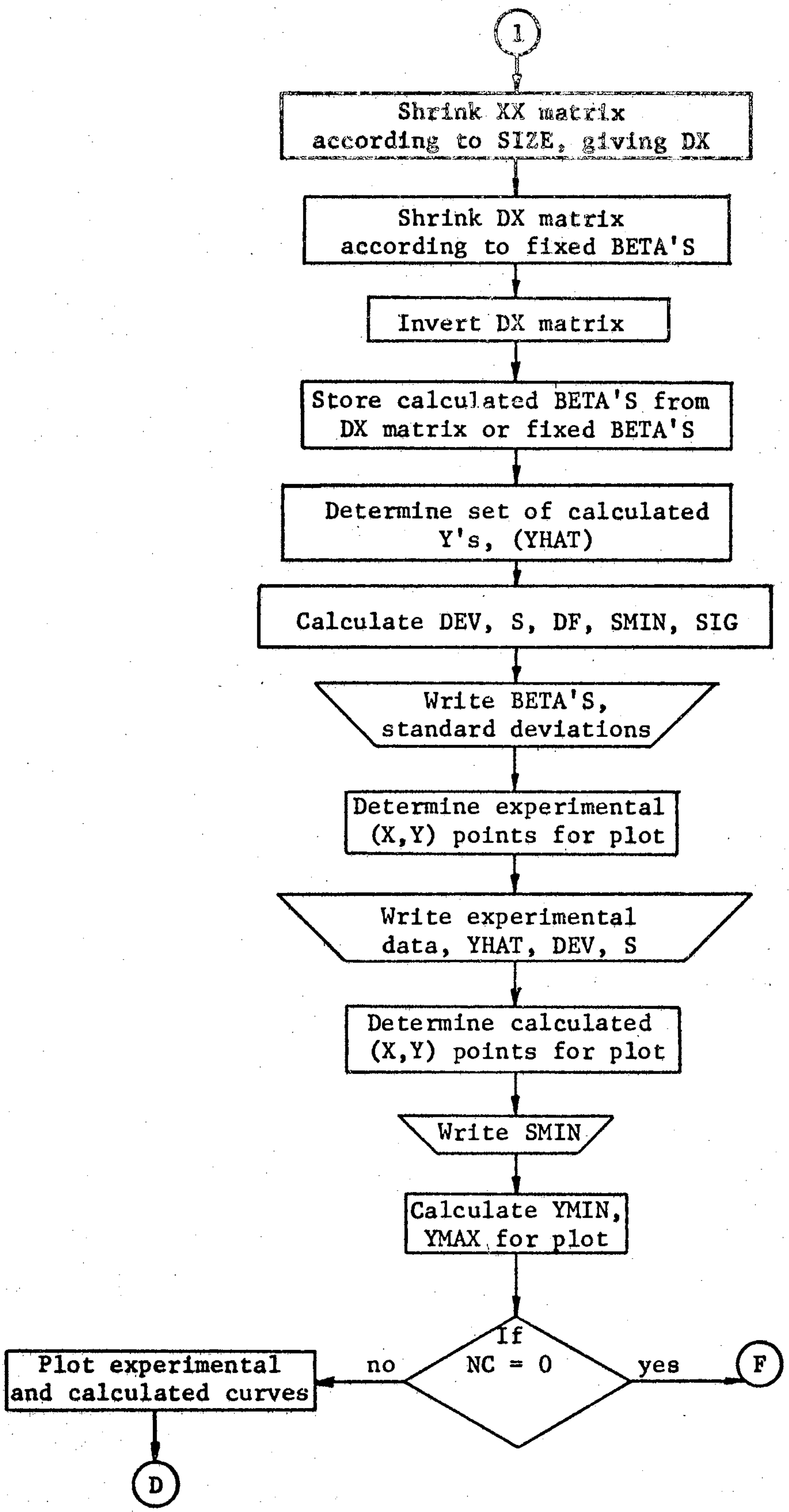
INPUT REQUIREMENTS FOR CORRESPONDING SOLUTIONS $\bar{n}$, [L] PROGRAM

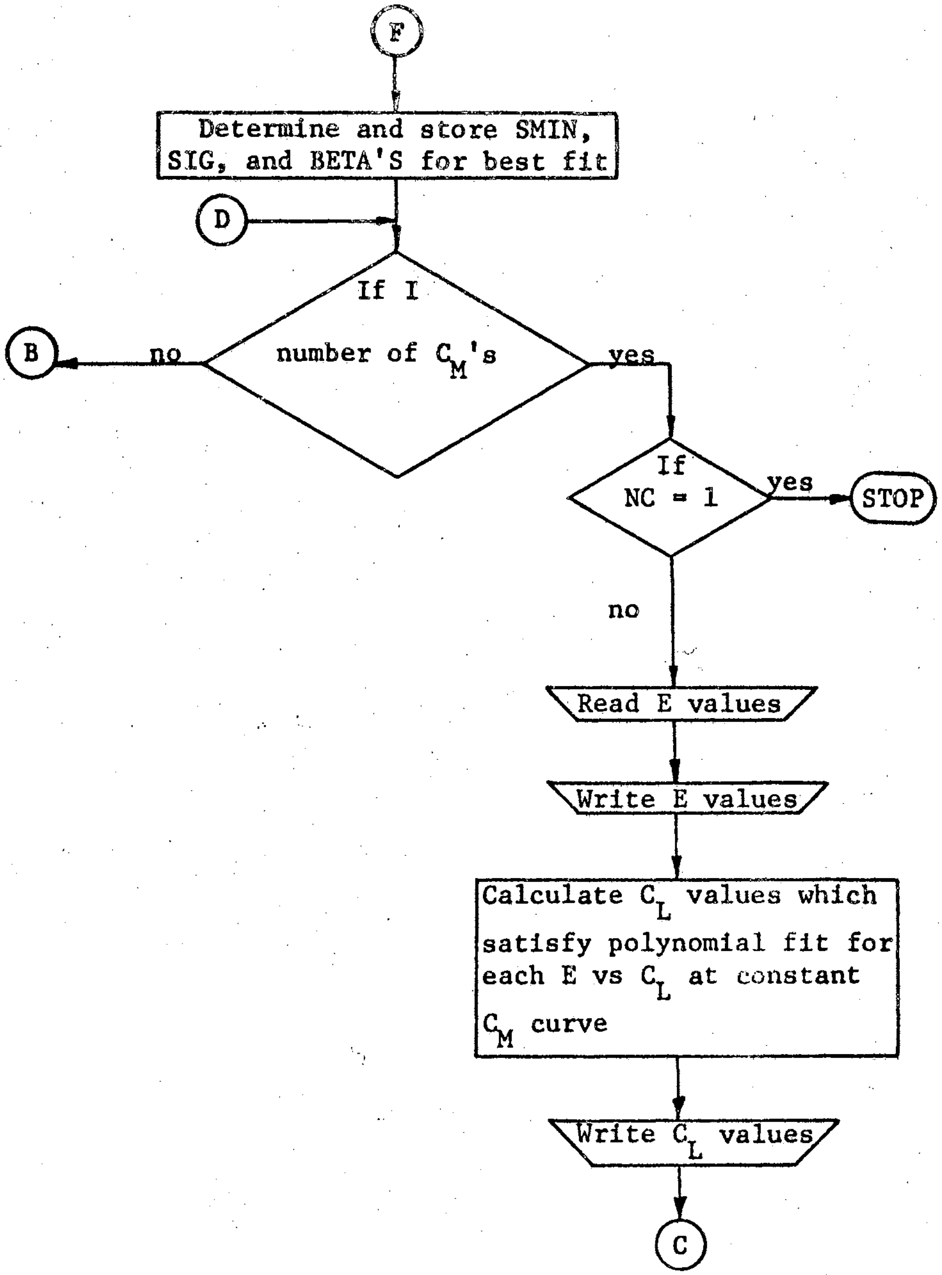
Card Number	Columns	Format	Variable Name and Function
1	1-80	20A4	HEAD - column headings for output table
2	1-80	20A4	TITLE - title for plot
3	Same as card 6, Table XXI		
4	1-55	55H	name of system being studied
5	1-3	I3	L - number of C_M's
	4-6	I3	MMM - number of E values, maximum of 40
	7-9	I3	MSIZE - maximum size polynomial used for curve fit
	10-12	I3	NCONT - number of control cards
	13-15	I3	MPT - If MPT$\geq$8, control cards specifying system models are read in separate from data. If MPT$\leq$8, control cards are read in with data.
6	Same as card 3, Table XXI		
7	1-3	I3	MM - number of C_L values for a particular C_M
	4-6	I3	SIZE - size polynomial used to fit data set
8	1-77	7D11.4	XA - C_L values for E vs C_L plots
9	1-77	7D11.4	YA - E values for E vs C_L plots
10	Same as card 2, Table XXI		

TABLE XXIII (Continued)

Card Number	Columns	Format	Variable Name and Function
11-14	Same formats as cards 7-10 except for a different C_M		
15-18	Same formats as cards 7-10 except for a different C_M		
19-22	Same formats as cards 7-10 except for a different C_M		
23-25	1-80	8D10.3	E - E values for interpolation
26	1-3	I3	SIZE - size of polynomial used
	4-6	I3	NCONT - number of control cards
27	Same format as card 10 - CONTL		
28	Same format as card 6 - Beta		


START
Read HEAD, TITLE, MOP, NCH, TAB1, and name of system being studied
Read L, MMM, MSIZE, NCONT, MPT
If MPT < 9
no
yes
Read CONTL
Read BETA'S
If NC = 0
yes
no
B
C
Read SIZE, CONTL
If NC = 1
no
yes
Read MM SIZE, XA, YA
Read CONTL
If MPT > 8
no
yes
Set XA's equal to C_M's
Read CONTL
Read BETA'S
If NC = 1
no
yes
Calculate XMIN, XMAX for plot
Calculate weight of data points
Build matrix, XX containing elements of normal equations
1


1
Shrink XX matrix according to SIZE, giving DX
Shrink DX matrix according to fixed BETA'S
Invert DX matrix
Store calculated BETA'S from DX matrix or fixed BETA'S
Determine set of calculated Y's, (YHAT)
Calculate DEV, S, DF, SMIN, SIG
Write BETA'S, standard deviations
Determine experimental (X,Y) points for plot
Write experimental data, YHAT, DEV, S
Determine calculated (X,Y) points for plot
Write SMIN
Calculate YMIN, YMAX for plot
If NC = 0
no
yes
F
Plot experimental and calculated curves
D


F
Determine and store SMIN, SIG, and BETA'S for best fit
D
If I
number of C_M's
no
B
yes
If
NC = 1
yes
STOP
no
Read E values
Write E values
Calculate C_L values which satisfy polynomial fit for each E vs C_L at constant C_M curve
Write C_L values
C

```
C     WILLIAM D. WAKLEY  OKLAHOMA STATE UNIVERSITY  CHEMISTRY DEPARTMENT
C     CORRESPONDING SOLUTIONS-LEAST SQUARES CURVE FIT AND PLOT   FORTRAN IV
C     IBM SYSTEM 360  OSU COMPUTER CENTER  30 DECEMBER 1969
C     CALCULATES BEST FIT OF E FUNCTIONS VS CL AT CONSTANT CM USING UP TO 7TH
C     DEGREE POLYNOMIALS.  INTERPOLATES AT SELECTED E VALUES AND CALCULATES
C     CORRESPONDING CL,CM VALUES.  FITS BEST LEAST SQUARES STRAIGHT LINE THROUGH
C     THESE POINTS AND CALCULATES THE SLOPE AND INTERCEPT FOR EACH E VALUE.
C     SLOPE=LIGAND NUMBER  INTERCEPT=FREE LIGAND CONCENTRATION
C     PROGRAM WILL PLOT EXPERIMENTAL AND CALCULATED CURVES IF DESIRED
      INTEGER CONTL,SIZE
      REAL*8 DABS,DSQRT
      DOUBLE PRECISION DX(8,9),XX(8,9),W,PIVOT,V(11,40),BETA(8),B(40,8),
     1SIG(40,8),YA(99,40),YHAT(40),DEV(40),S(40),X(40),Y(40),XA(99,40),E
     2(40),SMIN(40,127),SAVE(40,8),BB(40,8),CA(6,40),AY,SVE,YX,AYI,SUM,A
     3X,DDX
      DIMENSION HEAD(20),MOP(18),NCH(41),TITLE(20),TAB1(18),Z(1),CONTL(1
     127,8)
      COMMON TITLE,MOP,NCH,TAB1,ND,NP,NM,NB,JREAD5,JRITE6
    2 FORMAT(1P7D11.3)
    3 FORMAT(8I2)
    4 FORMAT(12I3)
    5 FORMAT(1X,20A4)
    6 FORMAT(20A4)
    7 FORMAT(55H
    8 FORMAT(88X,12HSMIN/(DF-1)=,D15.5)
   33 FORMAT(8D10.3)
   35 FORMAT(1P2D15.4/)
   36 FORMAT(1H ,6X,4HBETA,10X,7HSTD DEV)
   52 FORMAT(80A1)
   54 FORMAT(1H ,D10.3,2X,D15.5,2X,D10.3,2X,I3,2X,I3)
   57 FORMAT(7D11.4)
   63 FORMAT(4D10.3)
   81 FORMAT(8D10.3)
  111 FORMAT(7D10.3)
   69 FORMAT(1H ,1P1D15.5,2I3)
      JREAD5=5
      JRITE6=6
C     NC=0 FOR LEAST SQUARES FIT OF E VS CL,  NC=1 FOR FIT OF CL VS CM
      NC=0
C     READ HEADING FOR OUTPUT TABLE, TITLE OF PLOT, SYMBOLS USED FOR PLOT
      READ(JREAD5,6) (HEAD(I), I=1,20)
      READ(JREAD5,6) (TITLE(I), I=1,20)
      READ(JREAD5,52) (MOP(I), I=1,18),(NCH(I), I=1,40),(TAB1(I), I=1,18
     1),ND,NP,NM,NB
C     THE NAME OF THE SYSTEM BEING STUDIED IS READ IN HERE.
 1000 READ(JREAD5,7)
C     L=NUMBER OF CM, MAXIMUM=8  MMM=NUMBER OF E VALUES, MAXIMUM=40  MSIZE=8=
C     MAXIMUM SIZE OF POLYNOMIAL USED FOR CURVE FIT, IE 7TH DEGREE POLYNOMIAL
C     NCONT=NUMBER OF CONTROL CARDS, IE NUMBER OF MODELS MAXIMUM=127
C     MPT=IF(MPT.GT.8), CONTROL CARDS SPECIFYING SYSTEM MODELS ARE READ IN
C     SEPARATE FROM THE DATA.  IF(MPT.LE.8), CONTROL CARDS ARE READ IN WITH
C     THE (X,Y) DATA.
      READ(JREAD5,4) L,MMM,MSIZE,NCONT,MPT
      MS1=MSIZE+1
C     WRITE NAME OF SYSTEM BEING STUDIED
      WRITE(JRITE6,7)
      IF(MPT.LT.9)  GO TO 106
C     CONTL=CONTROL CARDS WHICH DETERMINE IF BETAS ARE TO BE FIXED OR CALCULATED
C     IF 0, THIS PARAMETER IS CALCULATED  IF 1, PARAMETER IS NOT CALCULATED
  110 DO  105  K=1,NCONT
  105 READ(JREAD5,3) (CONTL(K,I), I=1,MSIZE)
      IF(NC.EQ.0)  GO TO 106
C     SIZE=SIZE OF POLYNOMIAL
  107 READ(JREAD5,4)  SIZE,NCONT
      DO  101  K=1,NCONT
  101 READ(JREAD5,3)  (CONTL(K,I), I=1,MSIZE)
  112 DO  103  I=1,L
C     XA=CM*10**6 VALUES FOR CL VS CM PLOT
      XA(I,1)=0.100D+02
      XA(I,2)=0.200D+02
      XA(I,3)=0.300D+02
      XA(I,4)=0.400D+02
  103 CONTINUE
C     WRITE CONTROL PARAMETERS
      WRITE(JRITE6,4)  L,MMM,MSIZE,NCONT,MM
C     READ BETAS(COEFFICIENTS OF POLYNOMIAL)
  106 READ(JREAD5,33)  (BETA(I), I=1,MSIZE)
C     THROUGH STATEMENT 100 LEAST SQUARES FIT OF DATA
      DO  100  I=1,L
      IF(NC.EQ.1)  GO TO 1122
C     MM=NUMBER OF CL VALUES FOR EACH CM, MAXIMUM=40
  115 READ(JREAD5,4)  MM,SIZE
C     XA=CL*10**5 FOR E VS CL PLOT
      READ(JREAD5,57)  (XA(I,J), J=1,MM)
C     YA=E FUNCTIONS*10**3 FOR E VS CL PLOT
      READ(JREAD5,57)  (YA(I,J), J=1,MM)
      IF(MPT.GT.8)  GO TO 1122
  114 DO  104  K=1,NCONT
  104 READ(JREAD5,3)  (CONTL(K,NN), NN=1,MSIZE)
C     CALCULATES XMIN, XMAX FOR PLOT
 1122 XMIN=XA(I,1)
      DO 199 J=2,MM
      IF(XMIN.LT.XA(I ,J))  GO TO 199
   39 XMIN=XA(I ,J)
  199 CONTINUE
      XMAX=XA(I ,1)
      DO 99 J=2,MM
      IF(XMAX.GT.XA(I ,J))  GO TO 99
   38 XMAX=XA(1 ,J)
   99 CONTINUE
      XMAX=XMAX+0.2*(XMAX-XMIN)
      DO 10 K=1,MSIZE
      DO 10 J=1,MS1
   10 XX(K,J)=0.0D+00
C     CALCULATE WEIGHT OF DATA POINTS
      DO 12 J=1,MM
      W=1.0D+00
 2111 V(MSIZE+3,J)=W
 1111 V(1,J)=1.0D+00
   29 V(2,J)=XA(I ,J)
```

```
      DO 9 II=3,MSIZE
    9 V(II,J)=V(II-1,J)*XA(I ,J)
   27 V(MSIZE+1,J)=YA(I,J)
      V(MSIZE+2,J)=W
C     BUILD MATRIX CONTAINING ELEMENTS OF NORMAL EQUATIONS
      DO 12 II=1,MSIZE
      PIVOT=V(II,J)
      DO 12 JA=1,MS1
   12 XX(II,JA)=XX(II,JA)+W*PIVOT*V(JA,J)
   75 CONTINUE
      SVE=1.0D+05
C     SHRINK MATRIX ACCORDING TO SIZE
   13 DO 25  LL=1,NCONT
      II=1
      DO 16 K=1,SIZE
      JJ=1
      DO 15 J=1,SIZE
      IF(CONTL(LL  ,K).EQ.1)  GO TO 16
 1314 IF(CONTL(LL  ,J).EQ.1)  GO TO 15
 1315 DX(II,JJ)=XX(K,J)
      JJ=JJ+1
   15 CONTINUE
      II=II+1
   16 CONTINUE
C     SHRINK MATRIX ACCORDING TO FIXED BETA
      N=II-1
      M=II
      II=1
      DO 17 K=I,SIZE
      IF(CONTL(LL  ,K).EQ.1)  GO TO 17
 1717 AY=0.0D+00
      DO 22 J=I,SIZE
   22 AY=AY+BETA(J)*XX(K,J)
      DX(II,M)=XX(K,MS1)-AY
      II=II+I
   17 CONTINUE
C     INVERT MATRIX
   18 CALL INVERT(N,M,DX)
      KK=1
      DO 185 K=1,MSIZE
      IF(CONTL(LL  ,K).EQ.1)  GO TO 184
C     STORE CALCULATED BETA FROM MATRIX OR FIXED BETA
 1844 B(I,K)=DX(KK,M)
      KK=KK+1
      GO TO 185
  184 B(I,K)=BETA(K)
  185 CONTINUE
      SMIN(I,LL)=0.0D+00
C     DETERMINE SET OF CALCULATED BETAS
      DO 21 J=1,MM
      AY=0.0D+00
      DO 32 K=1,SIZE
   32 AY=AY+B(I,K)*V(K,J)
      YHAT(J)=AY
C     CALCULATE DEVIATION
      DEV(J)=V(MS1,J)-YHAT(J)
C     CALCULATE WEIGHTED SQUARE OF DEVIATIONS
      S(J)=V(MSIZE+2,J)*DEV(J)*DEV(J)
   21 SMIN(1,LL)=SMIN(I,LL)+S(J)
C     CALCULATE DEGREES OF FREEDOM
      DF=MM-N
  130 IF(MM.EQ.N)  GO TO 132
  131 IF(MM.EQ.N+1)  GO TO 132
C     CALCULATE GOODNESS-OF-FIT PARAMETER
  133 SMIN(I,LL)=SMIN(I,LL)/(DF-1)
  132 KK=1
C     CALCULATE STANDARD DEVIATION OF BETAS
      DO 188 K=1,MSIZE
      IF(CONTL(LL  ,K).EQ.1)  GO TO 187
 1877 AY1=DX(KK,KK)*SMIN(I,LL)
      AY=DABS(AY1)
      SIG(I,K)=DSQRT(AY)
 3131 KK=KK+1
      GO TO 188
  187 SIG(I,K)=0.0D+00
  188 CONTINUE
C     WRITE BETAS AND STANDARD DEVIATIONS
 3434 WRITE(JRITE6,36)
      WRITE(JRITE6,35) (B(I,K),SIG(I,K), K=1,SIZE)
C     WRITE HEADINGS
      WRITE(JRITE6,5) (HEAD(K), K=1,20)
C     DETERMINES EXPERIMENTAL (X,Y) POINTS FOR PLOT
      DO 23 K=1,MM
      X(K)=V(2,K)
      Y(K)=V(MS1,K)
C     WRITES 3 COLUMNS OF EXPERIMENTAL DATA, CALCULATED Y, DEVIATION, WEIGHTED
C     SUM OF SQUARES OF DEVIATIONS
   23 WRITE(JRITE6,2) V(2,K),V(MS1,K),V(MSIZE+3,K),V(MSIZE+2,K),YHAT(K),
     1DEV(K),S(K)
C     DETERMINES CALCULATED (X,Y) POINTS FOR PLOT
      DO 24 K=1,MM
      J=K+MM
      Y(J)=YHAT(K)
   24 X(J)=V(2,K)
C     WRITES GOODNESS-OF-FIT PARAMETER
      WRITE(JRITE6,8)  SMIN(1,LL)
      Z(1)=1.0
C     CALCULATE YMIN,YMAX FOR PLOT
      YMIN=Y(1)
      NPTS=MM+MM
      DO 399 J=2,NPTS
      IF(YMIN.LT.Y(J))  GO TO 399
   41 YMIN=Y(J)
  399 CONTINUE
      YMAX=Y(1)
      DO 299 J=2,NPTS
      IF(YMAX.GT.Y(J))  GO TO 299
   40 YMAX=Y(J)
  299 CONTINUE
      YMAX=YMAX+0.1*(YMAX-YMIN)
```

```
      IF(NC.EQ.0)  GO TO 117
  118 CALL PLOT(X,XMIN,XMAX,0,Y,YMIN,YMAX,0,Z,0.0,0.0,0,NPTS,2,1,0,2)
      IF(NC.EQ.1)  GO TO 25
  117 DO  189  K=1,SIZE
      YX=DABS(B(I,K))
C     IF STANDARD DEVIATION OF BETA IS GT BETA, GO TO NEXT MODEL
      IF(SIG(I,K).GT.YX)  GO TO 26
  189 CONTINUE
C     DETERMINE AND STORE BETAS, STANDARD DEVIATIONS, AND SMIN FOR 'BEST FIT'
   14 IF(SVE.LT.SMIN(I,LL))  GO TO 26
   30 SVE=SMIN(1,LL)
   19 DO  20  K=1,MSIZE
      BB(I,K)=B(1,K)
   20 SAVE(I,K)=SIG(I,K)
   26 CONTINUE
      1F(LL.EQ.NCONT)  SMIN(I,LL)=SVE
   25 CONTINUE
  100 CONTINUE
      IF(NC.EQ.1)  GO TO 109
      DO  116  I=1,L
C     WRITE BETAS, STANDARD DEVIATIONS, AND SMIN FOR 'BEST FIT'
  113 WRITE(JRITE6,36)
      WRITE(JRITE6,35) (BB(I,K),SAVE(I,K),K=1,MSIZE)
      WRITE(JRITE6,8)  SMIN(I,NCONT)
  116 CONTINUE
   28 MM=MMM
C     READ E VALUES FOR INTERPOLATION OF E VS CL CURVES
      READ(JREA05,81)  (E(J), J=1,MM)
      DO 46 J=1,MM
C     WRITE E VALUES
   46 WRITE(JRITE6,111) E(J)
C     INTERPOLATES E VS CL CURVES, DETERMINES CORRESPONDING VALUES OF CL,CM
C     MAXIMUM NUMBER OF E VALUES=40
      DO  74  J=1,MM
      DO  74  I=1,L
      DDX=0.1D+00
      AX=5.0D+01
   48 SUM=BB(I,1)+BB(I,2)*AX+BB(I,3)*AX**2+BB(I,4)*AX**3+BB(I,5)*AX**4+B
     1B(I,6)*AX**5+BB(I,7)*AX**6+BB(I,8)*AX**7
   49 IF(DABS(E(J)-SUM).LT.I.0D-04)  GO TO 47
  128 IF(SUM.GT.0.0D+00)  GO TO 126
  129 IF(SUM.LT.0.0D+00)  GO TO 127
  126 IF(E(J)-SUM) 61,47,62
  127 AX=AX+1.0
      GO TO 48
   61 AX=AX-DDX*AX
      GO TO 48
   62 AX=AX+DDX*AX
  125 DDX=DDX*0.5D+00
      GO TO 48
   47 CA(I,J)=AX
C     WRITES CL, INDEX OF CM, INDEX OF E VALUE
   74 WRITE(JRITE6,69)  CA(1,J),I,J
C     STORE CALCULATED CL'S IN YA FOR PLOT VS CM
      DO  108  I=1,L
      DO 108  J=1,MM
  108 YA(J,I)=CA(I,J)
      NC=1
      MM1=MM
      MM=L
      L=MM1
C     GO TO 107, PERFORM LEAST SQUARES CURVE FIT ON EACH CL,CM SET OF DATA
      GO TO 107
  109 CONTINUE
      STOP
      END
      SUBROUTINE INVERT(N,M,DX)
      DOUBLE PRECISION DX,PIVOT1,PIVOT2
      DIMENSION DX(8,9)
      DO 30 I=1,N
      PIVOT1=1.D0/DX(I,I)
      DX(I,I)=PIVOT1
      DO 10 J=1,M
      IF(J.EQ.I)  GO TO 10
 1010 DX(I,J)=PIVOT1*DX(I,J)
   10 CONTINUE
      DO 25 K=1,N
      IF(K.EQ.I)  GO TO 25
 2525 PIVOT2=DX(K,I)
      DX(K,I)=-PIVOT2*PIVOT1
      DO 20 L=1,M
      IF(L.EQ.I)  GO TO 20
 2020 DX(K,L)=DX(K,L)-PIVOT2*DX(I,L)
   20 CONTINUE
   25 CONTINUE
   30 CONTINUE
      RETURN
      END
C     SUBROUTINE PLOT AND SUBROUTINE POT ARE THE SAME AS SHOWN IN THE SPECIES
C     NUMBER PROGRAM
C
C     DATA
C
    X            Y            SIG  Y        W          YHAT       Y-YHAT   W(Y-YHAT)**2
      CORRESPONDING SOLUTIONS-LEAST SQUARES-PLOT
 E=FUNCTION(L)     .*                                          TOTAL LIGAND CONC .*-
   PCV-SN COMPLEXES
  4 21  8  1  7
 0.000D+00 0.000D+00 0.0000+00 0.000D+00 0.000D+00 0.0000+00 0.000D+00 0.000D+00
  7  7
 0.5000D+01 0.10000+02 0.2000D+02 0.3000D+02 0.4000D+02 0.5000D+02 0.6000D+02
 0.2943D+01 0.8886D+01 0.1547D+02 0.1616D+02 0.1664D+02 0.1673D+02 0.1641D+02
 0 0 0 0 0 0 0 1
  7  7
 0.5000D+01 0.1000D+02 0.2000D+02 0.3000D+02 0.4000D+02 0.5000D+02 0.6000D+02
 0.9714D+00 0.3843D+01 0.9836D+01 0.1553D+02 0.1537D+02 0.1526D+02 0.1526D+02
 0 0 0 0 0 0 0 1
  7  7
 0.6000D+01 0.1000D+02 0.2000D+02 0.3000D+02 0.4000D+02 0.5000D+02 0.6000D+02
 0.6038D+00 0.1295D+01 0.5624D+01 0.9986D+01 0.1421D+02 0.1494D+02 0.1507D+02
```

```
0 0 0 0 0 0 0 1
 7  7
0.6700D+01 0.1000D+02 0.2000D+02 0.2500D+02 0.3000D+02 0.4000D+02 0.5000D+02
0.4973D+00 0.9464D+00 0.3443D+01 0.5004D+01 0.6764D+01 0.1109D+02 0.1358D+02
0 0 0 0 0 0 0 1
0.300D+01 0.350D+01 0.400D+01 0.450D+01 0.500D+01 0.550D+01 0.600D+01 0.650D+01
0.700D+01 0.750D+01 0.800D+01 0.850D+01 0.900D+01 0.950D+01 0.100D+02 0.105D+02
0.110D+02 0.115D+02 0.120D+02 0.125D+02 0.130D+02
 2  1
0 0 1 1 1 1 1 1
0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00 0.000D+00
```

APPENDIX E

PROGRAM LISTING AND DATA SET FOR PIT-MAPPING PROGRAM

TABLE XXIV

INPUT REQUIREMENTS FOR PIT-MAPPING PROGRAM

Card Number	Columns	Format	Variable Name and Function
1	1-40	10A4	JACK - name of system being studied
2	1-10	F10.2	PKP1 - -log of trial stability constant
	11-20	F10.2	PKP2 - -log of trial stability constant
	21-30	F10.2	PKP3 - -log of trial stability constant
	31-33	I3	NUMPH - number of solutions
	34-39	F6.2	DEC - initial value of step matrix
	40-42	I3	JREP - number of repetitions
	43-45	I3	NN - number of constants calculated
	46-48	I3	NF - number of trial constants
	49-51	I3	JQ - number of species for which molar extinction coefficients are to be calculated
	52-54	I3	JNO - number of species for which molar extinction coefficients are known
	55-57	I3	NSP - number of wavelengths
3	1-50	5F10.2	LOGF - logs of trial stability constants
4	1-9	3I3	IPO - indexes of constants to be varied

TABLE XXIV (Continued)

Card Number	Columns	Format	Variable Name and Function
	10-18	3I3	JEQ - indexes of species for which molar extinction coefficients are to be calculated
5	1-10	E10.3	PXLT - C_L for ligand system, C_M for metal-ligand system
	11-70	10F6.2	PH - pH's of solutions
Next M cards	1-80	16(F4.3,1X)	SPEC - absorbance readings with number of cards determined by NUMPH and NSP. See Table XX for explanation of format.
Next N cards	1-80	16(F4.3,1X)	CK - baseline correction with number of cards determined by NSP. See Table XX for explanation of format.
Next card	1-80	20A4	TITLE - title for plot
Next card	1-18	80A1	MOP - title for Y-axis of plot
	19-21		NCH - symbols for plot
	59-76		TAB1 - title for X-axis of plot
	77		ND - "."
	78		NP - "+"
	79		NM - "-"
	80		NB - blank
Next card	1-80	8E10.3	ALNT - C_L for metal-ligand systems, zeros for ligand system

TABLE XXIV (Continued)

Card Number	Columns	Format	Variable Name and Function
Next MM cards	1-80	10(F6.1,2X)	EQ - known molar extinction coefficients with number of cards determined by JNO and NSP

```
C     PITMAPPING PROGRAM
      DIMENSION ALNT(10),PH(10),TIME(10),SPEC(97,10),XX(161),YY(321),
     1WT(97),JACK(10),AH(10),Q(9,10),EQ(9,97),X1(321),Y1(321),LOGF(5),PK
     2(8),DK(8),SQSX(16),WSX(8),PP(8),RR(8,8),VV(8),RINV(8,8),A(8,8),B
     3(8,8),WW(8,8),SH(8,8),EE(8,8),ALPH(10),UNT(5),CSPC(97,10),CK(80)
      DIMENSION XLAB(5),YLAB(5),GLAB1(5),GLAB2(5),UTX(5,6),U(5),VAL(5),
     1SPK(8),IMI(8),IPO(8),SIGV(8),JEQ(9)
      DIMENSION X(388),Y(388),Z(1),TITLE(20),MOP(18),NCH(41),TAB1(18)
      COMMON TITLE,MOP,NCH,TAB1,ND,NP,NM,NB
      REAL LOGF
      LOGICAL*1 TAG/.FALSE./,TEST/.FALSE./
      DATA IMI/8*0/,SIGV/8*1./,SPK/8*0./,Q/90*0./
   14 FORMAT(80A1)
   13 FORMAT(20A4)
C     NAME OF THE SYSTEM
      READ(5,101) JACK
  101 FORMAT(10A4)
C     PKP1,PKP2,PKP3-TRIAL STABILITY CONSTANTS, NUMPH-NUMBER OF SOLUTIONS, DEC-
C     INITIAL VALUE OF DIAGONAL STEP MATRIX, JREP-NUMBER OF REPETITIONS,
C     NN-NUMBER OF CONSTANTS CALCULATED, NF-NUMBER OF TRIAL CONSTANTS,
C     JQ-NUMBER OF SPECIES WHOSE MOLAR EXTINCTION COEFFICIENTS ARE TO BE
C     CALCULATED, JNO-NUMBER OF SPECIES WHOSE MOLAR EXTINCTION COEFFICIENTS
C     ARE KNOWN, NSP-NUMBER OF WAVELENGTHS
      READ(5,103) PKP1,PKP2,PKP3,NUMPH,DEC,JREP,NN,NF,JQ,JNO,NSP
  103 FORMAT(F10.2,F10.2,F10.2,I3,F6.2,I3,I3,I3,I3,I3,I3)
C     LOGF-LOG OF TRIAL STABILITY CONSTANTS
      READ(5,400) (LOGF(J), J=1,NF)
  400 FORMAT(5F10.2)
C     IPO-INDEX OF CONSTANTS TO BE VARIED, JEQ-INDEX OF SPECIES FOR WHICH
C     MOLAR EXTINCTION COEFFICIENTS ARE TO BE CALCULATED
      READ(5,401) (IPO(I),I=1,NN),(JEQ(J), J=1,JQ)
  401 FORMAT(17I3)
C     PXLT-CL FOR LIGAND SYSTEM, CM FOR LIGAND-METAL SYSTEM, PH=-LOG(H+)
      READ(5,100) PXLT,(PH(I), I=1,NUMPH)
  100 FORMAT(E10.3,10F6.2)
C     SPEC-ABSORBANCE READINGS, CK-BASELINE CORRECTION
      DO  7  I=1,NUMPH
    7 READ(5,102) (SPEC(K,I), K=1,NSP)
  102 FORMAT(16(F4.3,1X))
      READ(5,102) (CK(K), K=1,NSP)
      DO  22  I=1,NUMPH
      DO  22  K=1,NSP
      SPEC(K,I)=SPEC(K,I)-CK(K)
      IF(SPEC(K,I).LE.0.0) SPEC(K,I)=0.0
   22 CONTINUE
C     TITLE-TITLE FOR PLOT
      READ(5,13) (TITLE(I), I=1,20)
C     MOP-ORDINATE FOR PLOT, NCH-SYMBOLS FOR PLOT, TAB1-ABSCISSA FOR PLOT,
C     ND,NP,NM,NB-CONTROL PARAMETERS FOR PLOT
      READ(5,14) (MOP(I), I=1,18),(NCH(I), I=1,40),(TAB1(I), I=1,18),ND,
     1NP,NM,NB
C     ALNT-CL'S FOR METAL-LIGAND SYSTEM, ZEROS FOR LIGAND SYSTEM
      READ(5,19) (ALNT(I), I=1,NUMPH)
   19 FORMAT(8E10.3)
C     EQ-MOLAR EXTINCTION COEFFICIENTS
      READ(5,20) (EQ(1,K), K=1,NSP)
   20 FORMAT(10(F6.1,2X))
      DO  21  K=1,NSP
   21 EQ(2,K)=0.0
      WRITE(6,104)
  104 FORMAT(1H ,24H ANALYSIS OF SPECTRA M-L/62H PKA AND SPECTRA OF INDI
     1VIDUAL IONIC SPECIES BY SILLENS METHOD/)
      WRITE(6,101) (JACK(I), I=1,10)
      WRITE(6,105) PKP1,PKP2,PKP3,NUMPH
  105 FORMAT(1H0,8H PKA1   =,F10.3,8H PKA2   =,F10.3,8H PKA3   =,F10.3/8H N
     1UMPH =,I3/64H RANGE OF WAVELENGTH FROM 660 MU TO 265 MU WITH 5.0 M
     2U INTERVALS)
      WRITE(6,404) (LOGF(J), J=1,NF)
  404 FORMAT('0','TRIAL STAB.CONST,S..LOGF,S'/(5F10.3))
      WRITE(6,405) NN,(IPO(I), I=1,NN)
  405 FORMAT(' ','NO. OF CONSTANTS VARIED =',I3,'  I.E...PK(I),WHERE I=
     1',4(I3,','))
      WRITE(6,406) JQ,NSP,(JEQ(J), J=1,JQ)
  406 FORMAT(' ','MOL.EXT.COEF. FOR',I3,' SPECIES, I.E...EQ(J,K),K=1 TO'
     1,I3,',J=',4(I3,','))
      WRITE(6,209) JREP
  209 FORMAT(1H ,8H JREP   =,I3)
      WRITE(6,106) PXLT,(I,ALNT(I),I,PH(I), I=1,NUMPH)
  106 FORMAT(1H ,7H PXLT =,E11.4/(6H ALNT(,I2,3H) =,E11.4,4H PH(,I2,3H)
     1=,F8.3))
      WRITE(6,6) ((SPEC(K,I),I=1,NUMPH), K=1,NSP)
    6 FORMAT(1HJ, 7F12.7)
      DO  43  K=1,NSP
   43 WT(K)=1.0
C     PITMAP
      PK(1)=PKP1
      PK(2)=PKP2
      PK(3)=PKP3
      DO  450  J=1,NF
  450 PK(J+3)=-LOGF(J)
      NPK=NF+3
C     CALCULATES TRIAL STABILITY CONSTANTS
      DO  10  I=1,NPK
   10 DK(I)=EXP(-2.302585*PK(I))
      FKP3=1./DK(1)
      FKP2=1./DK(2)
      FKP1=1./DK(3)
      IF(FKP3.EQ.1.)  FKP3=0.0
      IF(FKP2.EQ.1.)  FKP2=0.0
C     CALCULATES (H+)
      DO  16  I=1,NUMPH
      AH(I)= EXP(-2.302585*PH(I))
      AHH=AH(I)
C     CALCULATES FRACTION OF LIGAND IN COMPLETELY DISSOCIATED FORM
   16 ALPH(I)=1./(((FKP1*FKP2*FKP3*AHH+FKP1*FKP2)*AHH+FKP1)*AHH+1.)
      UMIN=9999999.
      JJREP=0
      L=(NN+1)*(NN+2)/2
C     ASSIGN INITIAL VALUES TO EE AND SH-EE=IDENTITY MATRIX, SH=PRODUCT OF
C     TRIGONAL TWIST MATRIX, S, AND DIAGONAL STEP MATRIX, H
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```
      DO  26  J=1,NN
      DO  27  JK=1,NN
      IF(J-JK) 28,29,28
   28 EE(J,JK)=0.0
      SH(J,JK)=0.0
      GO TO 27
   29 EE(J,JK)=1.0
      SH(J,JK)=DEC
   27 CONTINUE
   26 CONTINUE
      CALL TWIST(SH,SQSX,NN,PP,RR,A,B,EE,WW,AH,ALPH,Q,PXLT,ALNT,DK,EQ,
     1SPEC,SQSD,NUMPH,NSP,WT,IPO,TAG,JEQ,JQ,JNO)
  204 JJREP=JJREP+I
      WRITE(6,602) ((SH(J,JK), JK=1,NN), J=1,NN)
  602 FORMAT(' ',' SH ='/(' ',3E15.7))
      CALL TWIST(SH,SQSX,NN,PP,RR,A,B,EE,WW,AH,ALPH,Q,PXLT,ALNT,DK,EQ,
     1SPEC,SQSO,NUMPH,NSP,WT,IPO,TAG,JEQ,JQ,JNO)
  510 DO  205  J=1,NN
      DO  206  JK=1,NN
      A(J,JK)=EE(J,JK)
      WW(J,JK)=RR(J,JK)
  206 CONTINUE
  205 CONTINUE
      WRITE(6,601) ((RR(J,JK), JK=1,NN), J=1,NN)
  601 FORMAT(' ',' RR ='/(' ',3E15.7))
C     CALCULATE VARIATION VECTOR TO OBTAIN CONSTANTS AT MINIMUM
      CALL MATIN(WW,NN,A,NN,DETER)
      DO  207  J=1,NN
      DO  208  JK=1,NN
      RINV(J,JK)=A(J,JK)
  208 CONTINUE
  207 CONTINUE
C     CALCULATE ERROR-SQUARE-SUM AT MINIMUM
      CALL PINUS(PP,RINV,NN,VV,1)
      XB=0.0
      DO 52 J=1,NN
      XB=XB+PP(J)*VV(J)
   52 CONTINUE
      XU=SQSX(I)-XB
      CALL PINUS(VV,B,NN,WSX,-1)
      NIMI=0
      NIPO=0
C     CALCULATE CONSTANTS AT MINIMUM
      DO  54  J=1,NN
      JJ=IPO(J)
      DK(JJ)=DK(JJ)*EXP(2.302585*WSX(J))
      PK(JJ)=PK(JJ)-WSX(J)
C     CHECK FOR NEGATIVE CONSTANTS
      IF(DK(JJ).GE.0.0)  GO TO 56
      NIMI=NIMI+1
      DK(JJ)=1.0
      PK(JJ)=-1.000
      IMI(NIMI)=JJ
      GO TO 54
   56 NIPO=NIPO+1
```

```
      IPO(NIPO)=JJ
   54 CONTINUE
      IF(NIMI.NE.0) CALL NIKO(B,RR,NN,EE,WW,A,XU,NIMI,IMI,NIPO,IPO,DK,PP
     1,SQSX(1),SH)
      IF(NIMI.NE.0)  GO TO 510
      WRITE(6,500) XU,(PK(I), I=1,NPK)
  500 FORMAT(' ',' CURRENT VALUES...XU=',E15.5,' PKS=',(8F11.3))
C     CALCULATE DEGREES OF FREEDOM
      XDF=NSP*(NUMPH-JQ)-NN
C     CALCULATE MOLAR EXTINCTION COEFFICIENTS AND U FOR THE 'BEST FIT' CONSTANTS
      CALL ECOEF(AH,ALPH,Q,PXLT,ALNT,DK,EQ,SPEC,SQSD,NUMPH,NSP,WT,TAG,NN
     1,JEQ,JQ,JNO)
C     CHECK TO SEE IF MIKO USED
      IF(IMI(1).NE.0)  GO TO 701
      IF(SQSD.GT.UMIN.OR.TAG)  GO TO 707
C     STORE INTERMEDIATE VALUES OF UD & THE PKS'S
  704 UMIN=SQSD
      DO  502  I=1,NPK
  502 SPK(I)=PK(I)
C     IF CURRENT CONSTANTS YIELD MINIMUM U AND ALL MOLAR EXTINCTION
C     COEFFICIENTS ARE POSITIVE, CALCULATION OF STANDARD DEVIATIONS (STATE-
C     MENT 705) AND OTHER OUTPUT BEGINS
  707 IF(JJREP.GE.JREP.OR.(ABS((SQSD-XU)/SQSD).LE.0.001.AND..NOT.TAG))
     1GO TO 705
      IF(TEST)  GO TO 204
      IF(TAG.OR.XU.LT.0.)  GO TO 507
C     CALCULATE SIGV
      XA=SQSD/XDF
      DO  505  J=1,NN
      T=XA*RINV(J,J)
      IF(T.LT.0.)  GO TO 506
      SIGV(J)=SQRT(T)*DEC
      GO TO 505
  506 IF(NN.EQ.1) SIGV(J)=SQRT(ABS(0.01*XU/PP(1)))*DEC
  505 CONTINUE
      WRITE(6,600) (SIGV(I), I=1,NN)
  600 FORMAT(' ','SIGV ='/(' ',E15.7))
  507 DO  508  J=1,NN
      DO  509  JK=1,NN
  509 SH(JK,J)=SH(JK,J)*SIGV(J)
  508 CONTINUE
      GO TO 204
  701 DO  703  J=1,NN
  703 SH(J,J)=DEC
      IMI(1)=0
      IF(TAG)  GO TO 204
      TEST=.TRUE.
      GO TO 704
C     CALCULATE STANDARD DEVIATION OF CONSTANTS
  705 CALL MULLE(RINV,B,NN,NN,NN,RR,0)
      CALL MULLE(B,RR,NN,NN,NN,A,1)
      XA=SQSD/XDF
      SDAB=SQRT(XA)
      DO  53  J=1,NPK
   53 PP(J)=0.000
```

```
      DO  55  J=1,NN
      JJ=IPO(J)
      XB=XA*A(J,J)
      IF(XB) 72,73,73
   72 PP(JJ)=-1.
      GO TO 55
   73 PP(JJ)=SQRT(XB)
   55 CONTINUE
      DO  51  J=4,NPK
   51 IF(PK(J).EQ.-1.000.OR.PK(J).EQ.0.000)  PP(J)=-1.000
C     OUTPUT SECTION- PRINT CONCENTRATIONS OF ALL SPECIES, MINIMUM VALUE OF
C     U, BEST SET OF CONSTANTS AND THEIR STANDARD DEVIATIONS
      WRITE(6,900) ((Q(J,I), J=1,8), I=1,NUMPH)
  900 FORMAT(' ','Q(J,I) ='/(' ',8E12.4))
      WRITE(6,520) UMIN,(SPK(I), I=1,NPK)
  520 FORMAT('0','UMIN=',E15.7,'  "BEST" PK,S',(8F11.3))
      WRITE(6,706) JJREP
  706 FORMAT('0',' NO.OF REPETITIONS=',I3)
      WRITE(6,201) SQSD,XU,DEC,(J,PK(J), J=1,NPK)
  201 FORMAT(1H0,8H SQSD  =,E15.7,6H XU  =,E15.7/6H DEC =,F10.3/(4H PK(,
     1I2,3H) =,F10.3))
      WRITE(6,202) SDAB,XA,(J,PP(J), J=1,NPK)
  202 FORMAT(1H ,6HSDAB =,E15.5/5H XA =,E11.4/20H STANDARD DEVIATIONS/(4
     1H PK(,I2,3H) =,F11.3))
      WRITE(6,210)
  210 FORMAT('0','      MOL. EXT. COEF. OF INDIVIDUAL SPECIES'/' ',' WAVE
     1LENGTH MU          ML            ML2         M2L '/)
  112 FORMAT(' ',6X,I3,6X,3E13.4)
C     PRINT MOLAR EXTINCTION COEFFICIENTS OF EACH SPECIES
      DO  8  K=1,NSP
      IW=665-K*5
      WRITE(6,112) IW,(EQ(J,K), J=3,5)
    8 CONTINUE
      DO  1  I=1,NUMPH
      WRITE(6,4)
    4 FORMAT(1H1,73H          SPEC                 CSPC                 SOLUTION #
     1          WAVELENGTH MU)
      DO  2  K=1,NSP
      IWV=665-K*5
      WA=EQ(1,K)*Q(1,I)
      DO  3  J=1,JQ
      JJ=JEQ(J)
    3 WA=WA+EQ(JJ,K)*Q(JJ,I)
      CSPC(K,I)=WA
    5 FORMAT(6X,F6.3,11X,F6.3,14X,I2,19X,I3)
C     PRINT EXPERIMENTAL AND CALCULATED SPECTRA
      WRITE(6,5) SPEC(K,I),CSPC(K,I),I,IWV
    2 CONTINUE
    1 CONTINUE
C     CALCULATE X AND Y COORDINATES, PLOT MOLAR EXTINCTION COEFFICIENTS
      NPLOT=JQ
      NPT=JQ*NSP
      I=1
      DO  9  J=1,JQ
      JJ=JEQ(J)
      DO  9  K=1,NSP
      Y(I)=EQ(JJ,K)*1.0E-02
      X(I)=665-K*5
      I=I+1
    9 CONTINUE
      XMAX=265.
      XMIN=660.
      YMIN=Y(1)
      DO  11  I=2,NPT
      IF(YMIN.LE.Y(I))  GO TO 11
      YMIN=Y(I)
   11 CONTINUE
      YMAX=Y(1)
      DO  12  I=2,NPT
      IF(YMAX.GE.Y(I))  GO TO 12
      YMAX=Y(I)
   12 CONTINUE
      CALLPLOT(X,XMIN,XMAX,0,Y,YMIN,YMAX,0,Z,ZMIN,ZMAX,0,NPT,NPLOT,1,0,2
     1)
      WRITE(6,15)
   15 FORMAT(1H ,2X,40HX=SN(H2PV)2+, *=SN(H2PV)2, .=SN2(H2PV)6+)
      STOP
      END
C
C
C
      SUBROUTINE TWIST(SH,S2,NN,PP,RR,AA,BB,EE,WW,A,B,Q,T1,T,DK,EQ,SP,
     1S1,N,M,WT,IPO,TAG,JEQ,JQ,JNO)
      DIMENSION SH(8,8),S2(16),WS(8),XA(8),PP(8),RR(8,8),AA(8,8),BB(8,8)
     1,EE(8,8),CC(8),DD(8),WW(8,8),A(10),B(10),Q(9,10),T(10),DK(8),
     2EQ(9,97),SP(97,10),WT(97),IPO(8),ISH(8),JEQ(9)
      LOGICAL*1 FLAG,TAG,ROW,COL
C     CALCULATE FIRST U VALUE FOR A GIVEN SET OF CONSTANTS
      CALL ECOEF(A,B,Q,T1,T,DK,EQ,SP,S1,N,M,WT,FLAG,NN,JEQ,JQ,JNO)
      S2(1)=S1
      TAG=FLAG
    5 DO  10  J=1,NN
      JJ=IPO(J)
   10 WS(J)=DK(JJ)
C     VARY EACH CONSTANT IN TURN, CALCULATE U FOR EACH CASE
      DO  11  J=1,NN
      DO  12  JK=1,NN
      JJ=IPO(JK)
   12 DK(JJ)=WS(JK)*EXP(2.302585*SH(JK,J))
      CALL ECOEF(A,B,Q,T1,T,DK,EQ,SP,S1,N,M,WT,FLAG,NN,JEQ,JQ,JNO)
      S2(J+1)=S1
   11 CONTINUE
      DO  13  J=1,NN
      DO  14  JK=1,NN
      JJ=IPO(JK)
   14 DK(JJ)=WS(JK)*EXP(-2.302585*SH(JK,J))
      CALL ECOEF(A,B,Q,T1,T,DK,EQ,SP,S1,N,M,WT,FLAG,NN,JEQ,JQ,JNO)
      JN=J+NN+1
      S2(JN)=S1
   13 CONTINUE
```

```
C     INSURES THE U(M,N) VALUES ARE ON UO SIDE OF UC
      NISH=0
      DO  50  J=1,NN
      JN=J+NN+1
      IF(S2(J+1).LE.S2(JN))  GO TO 50
      NISH=NISH+1
      ISH(NISH)=J
      DO  51  JK=1,NN
   51 SH(JK,J)=-SH(JK,J)
   50 CONTINUE
      IA=2*NN+1
      DO  15  J=1,NN
      DO  16  JK=1,NN
   16 XA(JK)=SH(JK,J)
      JL=J+1
      IF(JL-NN) 18,18,15
C     VARY TWO CONSTANTS SIMULTANEOUSLY CALCULATING A U VALUE FOR EACH CASE
   18 DO  19  JM=JL,NN
      DO  20  JK=1,NN
      XA(JK)=XA(JK)+SH(JK,JM)
      JJ=IPO(JK)
   20 DK(JJ)=WS(JK)*EXP(2.302585*XA(JK))
      CALL ECOEF(A,B,Q,T1,T,DK,EQ,SP,S1,N,M,WT,FLAG,NN,JEQ,JQ,JNO)
      IA=IA+1
      S2(IA)=S1
      DO  17  JK=1,NN
   17 XA(JK)=XA(JK)-SH(JK,JM)
   19 CONTINUE
   15 CONTINUE
      IF(NISH.EQ.0)  GO TO 42
      DO  40  J=1,NISH
      JJ=ISH(J)
      DO  41  JK=1,NN
   41 SH(JK,JJ)=-SH(JK,JJ)
   40 CONTINUE
   42 CONTINUE
C     CALCULATES DIAGONAL ELEMENTS OF PP, RR MATRICES
      DO  21  J=1,NN
      JN=NN+J+1
      WRITE(6,60) S2(J+1),S2(JN),S2(1)
   60 FORMAT(' ',' U+ =',E15.7,' U- =',E15.7,' UC =',E15.7)
      PP(J)=(S2(JN)-S2(J+1))/4.
      RR(J,J)=(S2(J+1)+S2(JN))/2.-S2(1)
   21 CONTINUE
C     CALCULATES OFF DIAGONAL ELEMENTS OF RR MATRIX
      DO  22  J=1,NN
      JL=J+1
      IF(JL-NN) 23,23,22
   23 IF(NISH.EQ.0)  GO TO 52
      ROW=.FALSE.
      DO  53  I=1,NISH
   53 IF(J.EQ.ISH(I)) ROW=.TRUE.
   52 DO  24  JK=JL,NN
      JM=(J+1)*NN-(J+1)*J/2+JK+1
      IF(NISH.EQ.0)  GO TO 55
      COL=.FALSE.
      DO  54  I=1,NISH
   54 IF(JK.EQ.ISH(I)) COL=.TRUE.
      IF(ROW.AND.COL)  GO TO 56
      IF(ROW.AND..NOT.COL)  GO TO 57
      IF(.NOT.ROW.AND.COL)  GO TO 58
   55 RR(J,JK)=(S2(JM)-S2(1))/2.+PP(J)+PP(JK)-(RR(J,J)+RR(JK,JK))/2.
      GO TO 59
   56 RR(J,JK)=(S2(JM)-S2(1))/2.-PP(J)-PP(JK)-(RR(J,J)+RR(JK,JK))/2.
      GO TO 59
   57 RR(J,JK)=(S2(1)-S2(JM))/2.+PP(J)-PP(JK)+(RR(J,J)+RR(JK,JK))/2.
      GO TO 59
   58 RR(J,JK)=(S2(1)-S2(JM))/2.-PP(J)+PP(JK)+(RR(J,J)+RR(JK,JK))/2.
   59 RR(JK,J)=RR(J,JK)
   24 CONTINUE
   22 CONTINUE
C     CALCULATE A CORRECTING TRIGONAL MATRIX W
      IF(NN.EQ.1)  GO TO 34
      NM=NN-1
      DO  25  II=1,NM
      DO  26  J=1,II
      DO  27  JK=1,II
      AA(J,JK)=RR(J,JK)
      BB(J,JK)=EE(J,JK)
   27 CONTINUE
   26 CONTINUE
      CALL MATIN(AA,II,BB,II,DETER)
      DO  28  JK=1,II
   28 CC(JK)=-RR(JK,II+1)
      CALL PINUS(CC,BB,II,DD,1)
      DO  29  JK=1,II
      WW(JK,II+1)=DD(JK)
   29 WW(II+1,JK)=0.0
   25 CONTINUE
   34 DO  30  II=1,NN
   30 WW(II,II)=1.0
      CALL MULLE(SH,WW,NN,NN,NN,AA,1)
C     STORE ORIGINAL SH MATRIX IN BB, PUT IMPROVED VARIATION MATRIX (AA) IN SH
      DO  31  J=1,NN
      DO  32  JK=1,NN
      BB(J,JK)=SH(J,JK)
      SH(J,JK)=AA(J,JK)
   32 CONTINUE
   31 CONTINUE
      DO  33  J=1,NN
      JJ=IPO(J)
   33 DK(JJ)=WS(J)
      RETURN
      END
C
C
C
      SUBROUTINE ECOEF(A,B,Q,T1,T,DK,EQ,SP,S1,N,M,WT,FLAG,NN,JEQ,JQ,JNO)
      DIMENSION A(10),B(10),Q(9,10),T(10),DK(8),EQ(9,97),SP(97,10),WT(97
     1),JEQ(9),C(4,10),EC(4,97)
```

```
      LOGICAL*1 FLAG
      FLAG=.FALSE.
      IF(B(1)) 20,20,18
   20 WRITE(6,109)
  109 FORMAT(' ',' USE SUBROUTINE ECOEF--LIGAND PITMAP')
      GO TO 19
   18 DO  10  I=1,N
      CALL EQUIL(A(1),B(I),Q,T1,T(I),DK,1)
   10 CONTINUE
C     LEAST SQUARE CALCULATION OF MOLAR EXTINCTION COEFFICIENTS
      S1=0.0
      IF(JQ.EQ.1)  GO TO 39
      SAA=0.0
      SAB=0.0
      SAC=0.0
      SAD=0.0
      SBB=0.0
      SBC=0.0
      SBD=0.0
      SCC=0.0
      SCD=0.0
      SDD=0.0
      KQ=JQ+1
C     CALCULATE CONCENTRATION MATRIX
      DO  21  I=1,N
      IF(JQ.EQ.4)  GO TO 24
      DO  23  J=KQ,4
   23 C(J,I)=0.0
   24 DO  5  J=1,JQ
      JJ=JEQ(J)
    5 C(J,I)=Q(JJ,I)
      SAA=SAA+C(1,I)**2
      SAB=SAB+C(1,I)*C(2,I)
      SAC=SAC+C(1,I)*C(3,I)
      SAD=SAD+C(1,I)*C(4,I)
      SBB=SBB+C(2,I)**2
      SBC=SBC+C(2,I)*C(3,I)
      SBD=SBD+C(2,I)*C(4,I)
      SCC=SCC+C(3,I)**2
      SCD=SCD+C(3,I)*C(4,I)
      SDD=SDD+C(4,I)**2
   21 CONTINUE
      IF(JQ-3) 30,28,27
C     FOUR SPECIES
   27 DETM=DETER4(SAA,SAB,SAC,SAD,SAB,SBB,SBC,SBD,SAC,SBC,SCC,SCD,SAD,
     1SBD,SCD,SDD)
      GO TO 34
C     THREE SPECIES
   28 DETM=DETER3(SAA,SAB,SAC,SAB,SBB,SBC,SAC,SBC,SCC)
      GO TO 34
C     TWO SPECIES
   30 DETM=SAA*SBB-SAB*SAB
   34 IF(DETM) 35,13,35
   13 WRITE(6,108)
  108 FORMAT(1H ,  ' DETM = 0.,CHECK MODEL')
   19 CALL EXIT
   35 DO  36  K=1,M
      SAU=0.0
      SBU=0.0
      SCU=0.0
      SDU=0.0
      DO  37  I=1,N
      WS=0.0
      DO  38  J=1,JNO
   38 WS=WS+EQ(J,K)*Q(J,I)
      S=SP(K,1)-WS
      SAU=SAU+C(1,I)*S
      SBU=SBU+C(2,I)*S
      SCU=SCU+C(3,I)*S
      SDU=SDU+C(4,I)*S
   37 CONTINUE
      IF(JQ-3) 44,46,45
C     TWO SPECIES
   44 DETM1=SAU*SBB-SBU*SAB
      DETM2=SAA*SBU-SAB*SAU
      EC(4,K)=0.0
      EC(3,K)=0.0
      GO TO 51
C     THREE SPECIES
   46 DETM1=DETER3(SAU,SBU,SCU,SAB,SBB,SBC,SAC,SBC,SCC)
      DETM2=DETER3(SAA,SAB,SAC,SAU,SBU,SCU,SAC,SBC,SCC)
      DETM3=DETER3(SAA,SAB,SAC,SAB,SBB,SBC,SAU,SBU,SCU)
      EC(4,K)=0.0
      GO TO 49
C     FOUR SPECIES
   45 DETM1=DETER4(SAU,SBU,SCU,SDU,SAB,SBB,SBC,SBD,SAC,SBC,SCC,SCD,SAD,
     1SBD,SCD,SDD)
      DETM2=DETER4(SAA,SAB,SAC,SAD,SAU,SBU,SCU,SDU,SAC,SBC,SCC,SCD,SAD,
     1SBD,SCD,SDD)
      DETM3=DETER4(SAA,SAB,SAC,SAD,SAB,SBB,SBC,SBD,SAU,SBU,SCU,SDU,SAD,
     1SBD,SCD,SDD)
      DETM4=DETER4(SAA,SAB,SAC,SAD,SAB,SBB,SBC,SBD,SAC,SBC,SCC,SCD,SAU,
     1SBU,SCU,SDU)
      EC(4,K)=DETM4/DETM
      IF(EC(4,K)) 48,49,49
C     CORRECTS FOR NEGATIVE MOLAR EXTINCTION COEFFICIENTS
   48 S1=S1+(T1*EC(4,K))**2*100.
   49 EC(3,K)=DETM3/DETM
      IF(EC(3,K)) 50,51,51
   50 S1=S1+(T1*EC(3,K))**2*100.
   51 EC(2,K)=DETM2/DETM
      IF(EC(2,K)) 52,53,53
   52 S1=S1+(T1*EC(2,K))**2*100.
   53 EC(1,K)=DETM1/DETM
      IF(EC(1,K)) 54,36,36
   54 S1=S1+(T1*EC(1,K))**2*100.
   36 CONTINUE
      GO TO 31
C     ONE SPECIES
   39 JJ=JEQ(1)
```

```
      DO  60   K=1,M
      WP=0.0
      WQ=0.0
      DO  61   I=1,N
      WS=0.0
      DO  62   J=1,JNO
   62 WS=WS+EQ(J,K)*Q(J,I)
      WP=WP+(SP(K,I)-WS)
   61 WQ=WQ+Q(JJ,I)
      EC(1,K)=WP/WQ
   60 IF(EC(1,K).LT.0.) S1=S1+(T1*EC(1,K))**2*100.
   31 IF(S1.NE.0.) FLAG=.TRUE.
C     CALCULATE ERROR-SQUARE-SUM
      DO  55   I=1,N
      DO 56   K=1,M
      WS=0.0
      DO  32   J=1,JQ
      JJ=JEQ(J)
      EQ(JJ,K)=EC(J,K)
   32 WS=WS+EQ(JJ,K)*Q(JJ,I)
      DO  33   J=1,JNO
   33 WS=WS+EQ(J,K)*Q(J,I)
   56 S1=S1+(SP(K,I)-WS)**2*WT(K)
   55 CONTINUE
      RETURN
      END
C
C
C
      SUBROUTINE MIKO(B,RR,NN,EE,WW,A,XU,NIMI,IMI,NIPO,IPO,DK,PP,SQ,SH)
      WRITE(6,1)
    1 FORMAT(1H ,17HNEGATIVE CONSTANT)
    2 CALL EXIT
      RETURN
      END
C
C
C
      FUNCTION DETER3(AA,AB,AC,BA,BB,BC,CA,CB,CC)
C     EVALUATES 3RD ORDER DETERMINANTS
      DETER3=AA*(BB*CC-BC*CB)-AB*(BA*CC-BC*CA)+AC*(BA*CB-BB*CA)
      RETURN
      END
C
C
C
      FUNCTION DETER4(AA,AB,AC,AD,BA,BB,BC,BD,CA,CB,CC,CD,DA,DB,DC,DD)
C     EVALUATES 4TH ORDER DETERMINANTS
      DETER4=AA*DETER3(BB,BC,BD,CB,CC,CD,DB,DC,DD)-AB*DETER3(BA,BC,BD,CA
     1,CC,CD,DA,DC,DD)+AC*DETER3(BA,BB,BD,CA,CB,CD,DA,DB,DD)-AD*DETER3(
     2BA,BB,BC,CA,CB,CC,DA,DB,DC)
      RETURN
      END
C
C
```

```
C
      SUBROUTINE NEWTRS(X,J,FX,DERIV)
C     SOLVES FOR CONCENTRATIONS OF SPECIES USING NEWTON'S METHOD
      J=J+1
      IF(J.NE.1)  GO TO 2
    1 T=1.0
    3 RETURN
    2 XP=X-FX/DERIV
      IF(ABS((XP-X)/(XP+X)).LT.1.0E-3)  GO TO 4
    5 X=XP
      T=T+1.
      IF(T.LE.50.0)  GO TO 3
    4 J=0
      X=XP
      RETURN
      END
C
C
C
      SUBROUTINE MATIN(A,N,B,M,DETER)
C     MATRIX INVERSION
      DIMENSION IPIVO(10),A(8,8),B(8,8),INDEX(10,2),PIVOT(10)
      EQUIVALENCE (IROW,JROW), (ICOLU,JCOLU), (AMAX,T,SWAP)
C     INITIALIZATION
   10 DETER=1.0
   15 DO  20  J=1,N
   20 IPIVO(J)=0
   30  DO  550  I=1,N
C     SEARCH FOR PIVOT ELEMENT
   40 AMAX=0.0
   45 DO  105  J=1,N
   50 IF(IPIVO(J)-1) 60,105,60
   60  DO  100  K=1,N
   70 IF(IPIVO(K)-1) 80,100,740
   80 IF(ABS(AMAX)-ABS(A(J,K))) 85,100,100
   85 IROW=J
   90 ICOLU=K
   95 AMAX=A(J,K)
  100 CONTINUE
  105 CONTINUE
  110 IPIVD(ICOLU)=IPIVO(ICOLU)+1
C     INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL
  130 IF(IROW-ICOLU) 140,260,140
  140 DETER=-DETER
  150 DO  200  L=1,N
  160 SWAP=A(IROW,L)
  170 A(IROW,L)=A(ICOLU,L)
  200 A(ICOLU,L)=SWAP
  205 IF(M) 260,260,210
  210 DO  250  L=1,M
  220 SWAP=B(IROW,L)
  230 B(IROW,L)=B(ICOLU,L)
  250 B(ICOLU,L)=SWAP
  260 INDEX(I,1)=IROW
  270 INDEX(I,2)=ICOLU
```

```
  310 PIVOT(I)=A(ICOLU,ICOLU)
  320 DETER=DETER*PIVOT(I)
C     DIVIDE PIVOT ROW BY PIVOT ELEMENT
  330 A(ICOLU,ICOLU)=1.0
  340 DO  350  L=1,N
  350 A(ICOLU,L)=A(ICOLU,L)/PIVOT(I)
  355 IF(M) 380,380,360
  360 DO  370  L=1,M
  370 B(ICOLU,L)=B(ICOLU,L)/PIVOT(I)
C     REDUCE NON-PIVOT ROWS
  380 DO  550  L1=1,N
  390 IF(L1-ICOLU) 400,550,400
  400 T=A(L1,ICOLU)
  420 A(L1,ICOLU)=0.0
  430 DO  450  L=1,N
  450 A(L1,L)=A(L1,L)-A(ICOLU,L)*T
  455 IF(M) 550,550,460
  460 DO  500  L=1,M
  500 B(L1,L)=B(LI,L)-B(ICOLU,L)*T
  550 CONTINUE
C     INTERCHANGE COLUMNS
  600 DO  710  I=1,N
  610 L=N+1-I
  620 IF(INDEX(L,1)-INDEX(L,2)) 630,710,630
  630 JROW=INDEX(L,1)
  640 JCOLU=INDEX(L,2)
  650 DO  705  K=1,N
  660 SWAP=A(K,JROW)
  670 A(K,JROW)=AIK,JCOLU)
  700 A(K,JCOLU)=SWAP
  705 CONTINUE
  710 CONTINUE
  740 RETURN
      END
C
C
C
      SUBROUTINE MULLE(AMAT,BMAT,NRAD,NMEL,NKOL,CMAT,IFRAM)
C     MATRIX MULTIPLICATION
      DIMENSION AMAT(8,8),BMAT(8,8),CMAT(8,8)
      DO  10  I=1,NRAD
      DO  20  J=1,NKOL
      W=0.0
      DO  30  M=1,NMEL
      IF(IFRAM-1) 12,11,12
   11 W=W+AMAT(I,M)*BMAT(M,J)
      GO TO 30
   12 IF(IFRAM) 14,13,14
   13 W=W+AMAT(I,M)*BMAT(J,M)
      GD TO 30
   14 W=W+AMAT(M,I)*BMAT(M,J)
   30 CONTINUE
      CMAT(I,J)=W
   20 CONTINUE
   10 CONTINUE
```

```
      RETURN
      END
C
C
C
      SUBROUTINE PINUS(PINNE,AMAT,N,PONNE,IFRAM)
C     MULTIPLICATION OF A MATRIX AND A VECTOR
      DIMENSION AMAT(8,8),PINNE(8),PONNE(8)
      DO  10  I=1,N
      W=0.0
      DO  20  J=1,N
      IF(IFRAM-1) 12,11,12
   11 W=W+PINNE(J)*AMAT(J,I)
      GO TO 20
   12 W=W+AMAT(I,J)*PINNE(J)
   20 CONTINUE
      PONNE(I)=W
   10 CONTINUE
      RETURN
      END
C
C
C
      SUBROUTINE EQUIL(X,Y,Q,T1,T2,DK,I)
C     DETERMINE CONCENTRATIONS OF SPECIES USING NEWTON'S METHOD AND AN
C     ITERATIVE PROCEDURE.  MODEL= ML, ML2, M2L
      DIMENSION Q(9,10), DK(8), NNSN(900), NNL(900)
      DATA NNSN/900*0/,NNL/900*0/
      J=0
      K=0
C     TRIAL CONSTANTS
      B1=DK(1)/X
      B2=DK(2)/(X*X)
      B3=DK(3)/X
      Q(1,I)=T2
      Q(2,I)=T1
    1 NQ=0
      K=K+1
      NSN=0
      ASN=Q(2,I)
    2 NQ=NQ+1
C     CALCULATE CONCENTRATIONSS OF 'FREE' LIGAND
      CALL NEWTRS(Q(1,I),J,FX,DFX)
      FX=Q(1,I)+B1*ASN*Q(1,I)+2.*B2*ASN*Q(1,I)*Q(1,I)+B3*ASN**2*Q(1,I)-T
     12
      DFX=1.+B1*ASN+4.*B2*ASN*Q(1,I)+B3*ASN**2
      IF(J.GT.0)  GO TO 2
      NNL(K)=NQ
      IF(Q(1,I).LT.0.0.OR.Q(1,I).GT.T2.OR.NQ.GE.51)  GO TO 4
    3 NSN=NSN+1
C     CALCULATE CONCENTRATION OF FREE METAL
      CALL NEWTRS(Q(2,I),J,FZ,DFZ)
      FZ=Q(2,I)+B1*Q(2,I)*Q(1,I)+B2*Q(2,I)*Q(1,I)*Q(1,I)+2.*B3*Q(2,I)*Q(
     12,I)*Q(1,I)-T1
      DFZ=1.+B1*Q(1,I)+B2*Q(1,I)*Q(1,I)+4.*B3*Q(2,I)*Q(1,I)
```

```
      IF(J.GT.0)  GO TO 3
      NNSN(K)=NSN
      IF(Q(2,I).LT.0.0.OR.Q(2,1).GT.T1.OR.NSN.GE.51)  GO TO 4
      IF(ABS((Q(2,I)-ASN)/(Q(2,I)+ASN)).GT.1.0E-03)  GO TO 1
C     CONCENTRATION OF ML
      Q(3,I)=B1*Q(2,1)*Q(1,I)
C     CONCENTRATION OF ML2
      Q(4,I)=B2*Q(2,I)*Q(1,I)*Q(1,I)
C     CONCENTRATION OF M2L
      Q(5,I)=B3*Q(2,I)*Q(2,I)*Q(1,I)
      WRITE(6,980) (NNL(J), J=1,K)
  980 FORMAT('0',' NQ =',(25I3))
      WRITE(6,990) (NNSN(J), J=1,K)
  990 FORMAT(' ',' NSN =',(25I3))
      RETURN
    4 WRITE(6,10)
   10 FORMAT('0',' ROOT APPROXIMATED IS INADEQUATE')
      WRITE(6,900) (Q(J,I), J=1,8)
  900 FORMAT(' ','Q(J,1) ='/(' ',8E12.4))
      WRITE(6,980) (NNL(J), J=1,K)
      WRITE(6,990) (NNSN(J), J=1,K)
      CALL EXIT
      END
C
C
C
C     SUBROUTINE PLOT ANO SUBROUTINE POT ARE THE SAME AS SHOWN IN THE SPECIES
C     NUMBER PROGRAM
C
C     DATA
C
      SN-PCV SERIES III
     -7.80     -14.74     -13.00  7  0.10  5  3  3  3  2 80
      0.00       0.00       0.00
  1  2  3  3  4  5
 3.000E-05  3.00  3.00  3.00  3.00  3.00  3.00  3.00
0045 0053 0063 0075 0086 0096 0105 0112 0119 0124 0127 0128 0128 0128 0127 0125
0124 0120 0119 0113 0109 0103 0096 0088 0079 0072 0065 0058 0055 0051 0050 0048
0048 0046 0047 0048 0048 0049 0050 0050 0051 0051 0051 0052 0053 0053 0054 0054
0053 0052 0051 0050 0050 0051 0052 0055 0058 0063 0068 0070 0070 0070 0072 0069
0067 0068 0069 0071 0072 0074 0078 0081 0085 0090 0089 0089 0084 0082 0082 0082
0055 0071 0085 0100 0115 0131 0148 0159 0171 0180 0188 0194 0197 0200 0203 0206
0207 0209 0209 0210 0204 0198 0186 0172 0156 0137 0120 0109 0089 0090 0083 0079
0077 0073 0071 0071 0071 0072 0072 0074 0074 0074 0075 0076 0077 0078 0079 0079
0078 0077 0075 0072 0070 0069 0071 0074 0080 0088 0092 0095 0093 0090 0089 0084
0081 0079 0082 0084 0088 0089 0094 0100 0110 0120 0123 0119 0114 0108 0102 0100
0088 0108 0128 0152 0177 0202 0226 0250 0275 0298 0317 0334 0348 0361 0378 0398
0421 0451 0489 0532 0562 0576 0556 0518 0461 0398 0340 0291 0252 0223 0200 0180
0166 0153 0146 0139 0134 0132 0130 0130 0129 0128 0127 0127 0128 0130 0132 0136
0138 0139 0138 0137 0133 0136 0139 0147 0159 0172 0180 0179 0167 0151 0137 0120
0111 0108 0112 0119 0127 0133 0145 0163 0194 0226 0232 0218 0203 0188 0175 0169
0102 0125 0145 0167 0189 0214 0239 0267 0293 0324 0351 0376 0403 0431 0468 0511
0572 0648 0738 0836 0913 0946 0929 0872 0786 0686 0587 0491 0416 0359 0317 0281
0252 0229 0213 0201 0193 0186 0182 0179 0176 0174 0173 0171 0173 0176 0182 0188
0196 0199 0199 0198 0198 0200 0208 0223 0241 0257 0264 0256 0229 0203 0178 0156
```

```
0141 0137 0145 0158 0168 0178 0197 0225 0276 0328 0338 0313 0291 0269 0247 0237
0118 0140 0162 0182 0203 0224 0246 0276 0306 0339 0371 0408 0445 0488 0541 0608
0701 0821 0969 1104 1224 1278 1262 1193 1087 0951 0812 0686 0576 0491 0429 0381
0341 0308 0286 0268 0257 0249 0243 0239 0236 0233 0232 0231 0233 0237 0244 0256
0265 0270 0270 0269 0268 0273 0284 0301 0327 0345 0347 0328 0293 0253 0222 0194
0176 0173 0182 0200 0214 0228 0249 0288 0358 0428 0442 0411 0385 0357 0331 0314
0143 0166 0190 0213 0232 0257 0281 0312 0348 0382 0418 0458 0500 0550 0609 0687
0797 0921 1066 1210 1321 1371 1348 1271 1158 1025 0872 0739 0631 0547 0487 0441
0407 0378 0362 0351 0348 0349 0350 0352 0353 0356 0358 0359 0361 0365 0370 0378
0382 0381 0376 0367 0362 0361 0368 0385 0405 0420 0420 0397 0357 0313 0278 0247
0228 0228 0238 0256 0269 0286 0313 0359 0438 0518 0529 0504 0474 0455 0420 0399
0149 0177 0199 0222 0242 0268 0293 0319 0354 0389 0424 0462 0502 0549 0609 0686
0788 0923 1062 1209 1335 1387 1368 1295 1187 1051 0913 0776 0668 0592 0539 0499
0473 0456 0447 0448 0454 0465 0478 0488 0498 0507 0513 0517 0519 0520 0522 0522
0519 0511 0496 0480 0466 0456 0456 0466 0482 0491 0489 0463 0420 0378 0339 0306
0287 0286 0296 0311 0327 0341 0366 0411 0488 0572 0601 0594 0585 0558 0512 0474
0000 0000 0001 0001 0002 0003 0004 0005 0006 0006 0007 0008 0008 0008 0008 0009
0010 0010 0011 0012 0013 0014 0014 0014 0015 0015 0016 0016 0017 0018 0019 0019
0019 0019 0020 0020 0020 0020 0021 0021 0021 0021 0021 0021 0021 0022 0022 0022
0023 0024 0024 0024 0025 0027 0029 0031 0033 0035 0037 0039 0041 0048 0052 0052
0051 0051 0051 0050 0049 0048 0046 0044 0043 0042 0040 0039 0038 0037 0037 0038
      EXTINCTION COEFFICIENTS FOR SN-PCV COMPLEXES IN 1M CL-
 EXT.COEFF.*10**-2X*.                                       WAVELENGTH IN MU  .+-
 0.600E-05 1.000E-05 2.000E-05 3.000E-05 4.000E-05 5.000E-05 6.000E-05
000286  000286  000143  000286  000286  000286  000286  000286  000429  000429
000286  000143  000143  000286  000429  000571  001143  001714  002429  003429
004143  005429  007714  010143  013000  017000  021857  027429  033143  040857
050714  058571  068714  080714  093857  104857  117857  129714  140429  150429
159571  166857  171000  174000  173857  171429  166571  160714  152000  143429
133000  123143  112429  103000  094286  087143  080714  075286  071429  067857
065286  063429  062286  061143  061000  060429  060286  060429  061286  062429
063714  064714  066714  071571  080714  096143  107857  106000  095143  079429
```

EQUIL for Ligand Systems

```
SUBROUTINE EQUIL(X,Y,Q,T1,T2,DK,I)
DIMENSION Q(9,10),DK(8)
FKP3=1./DK(1)
FKP2=1./DK(2)
FKP1=1./DK(3)
IF(FKP3.EQ.1.) FKP3=0.0
IF(FKP2.EQ.1.) FKP2=0.0
XALPH=1./(1.+X*FKP1+X*X*FKP1*FKP2+X*X*X*FKP1*FKP2*FKP3)
XB=T1*XALPH
Q(1,I)=XB
Q(2,I)=XB*X*FKP1
Q(3,I)=XB*X*X*FKP1*FKP2
Q(4,I)=XB*X*X*X*FKP1*FKP2*FKP3
RETURN
END
```

APPENDIX F

STABILITY CONSTANTS OF TIN-PYROCATECHOL VIOLET COMPLEXES FROM COMPUTER ANALYSIS OF SPECTRAL DATA

Abstract

Six computer programs have been collected, modified, or written and used to interpret absorbance data. These programs constitute a powerful method for analyzing spectrophotometric data obtained from systems containing mononuclear, polynuclear, or a mixture of mononuclear and polynuclear complexes. Three acid dissociation constants of pyrocatechol violet in 1M Cl^- solutions were determined with $pK_1 = 0.261 \pm 0.003$, $pK_2 = 7.508 \pm 0.001$, and $pK_3 = 8.332 \pm 0.003$. Molar extinction coefficients of pyrocatechol violet species were calculated. Spectrophotometric data from 1M Cl^- solutions of tin(IV) and pyrocatechol violet have been interpreted on the basis of the formation of 1:1, 1:2, and 2:1 metal-ligand complexes with $\log \beta_{11} = 7.801 \pm 0.133$, $\log \beta_{12} = 14.899 \pm 0.297$, and $\log \beta_{21} = 12.922 \pm 0.342$. Molar extinction coefficients of tin(IV)-pyrocatechol violet complexes were calculated.

Introduction

Studies of the absorption of visible and ultraviolet radiation have long been used to obtain information about equilibria in solution. However, since the optical absorbance of a solution is governed by a characteristic intensive factor, the extinction coefficient, as well as by the concentration of each absorbing species, interpretation of measurements of this type is complicated if several complexes coexist. Many spectrophotometric methods used in quantitative analysis have been developed without complete knowledge of the nature and properties of the absorbing species. Therefore, unambiguous methods for the determination of the number, nature, and stabilities of several absorbing species in solution are needed.

When systems composed of several complexes in equilibrium are studied by spectrophotometry, equations describing the systems are usually nonlinear in the unknown coefficients. Least squares curve fitting, iterative calculations, the method of continuous variations, and other graphical methods often used in these studies attempt to determine two or three of these parameters in a single experiment or a single calculation. Except in the simplest cases, the accuracy and precision of the experimental data are not sufficient to produce unambiguous results.

Experimental

Apparatus. All glassware used was Pyrex and volumetric glassware met ACS requirements. Only Class A volumetric glassware was used. Scientific Cell Company fused silica cells were used. The matched silica cells were rectangular with a one centimeter path length.

Instruments. All weighings were performed on a Mettler Type H5 balance. Samples were weighed to ± 0.001 grams. A Beckman Zeromatic pH meter equipped with a Sargent/Jena S-30080-15C saturated calomel reference electrode and a Sargent/Jena S-30050-15C glass electrode was used for all pH measurements. The pH meter was standardized before use with buffers prepared from pHydrion Buffer powders. Absorbance measurements were made with a Cary Recording Spectrophotometer, Model 14. All measurements were made in the visible or ultraviolet regions of the spectrum. Absorbance readings were taken from the spectra of the solutions at 50 Å intervals. All readings were estimated to ± 0.001

absorbance units. These absorbance readings were then punched on computer cards for analysis.

Reagents. Distilled H_2O which had been passed through a mixed cation-anion exchange resin was used throughout. The pyrocatechol violet (PCV or 3,3',4'-trihydroxyfuchsone-2"-sulfonic acid) was Eastman reagent grade. Stock solutions of PCV were prepared by dissolving appropriate amounts of the reagent in distilled H_2O. Baker Analyzed Reagent grade sodium stannate, $Na_2SnO_3 \cdot 3H_2O$, was heated at 160°C for approximately 24 hours to remove water of hydration. Stock Sn(IV) solutions were prepared by dissolving Na_2SnO_3 in 6.13M HCl. Baker Analyzed Reagent grade hydrochloric acid was used for solution preparation and sodium chloride solutions were used to provide a constant ionic medium.

Pyrocatechol Violet Solutions. Visible and ultraviolet spectra of aqueous solutions of pyrocatechol violet at a fixed concentration of 8×10^{-5}M but of different pH's were recorded. The pH was varied from 0.42 to 8.18 using appropriate amounts of HCl or NaOH solutions. Solution pH was measured just prior to recording of the spectra. The ionic strength was held constant by maintaining the Cl^- concentration at 1M. Solution compositions are given in Table III and the spectra in Figures 5 and 6.

The spectra of another series of PCV solutions were determined with the PCV concentrations ranging from 2×10^{-5}M to 7×10^{-5}M in 1M Cl^- media. The pH of each solution was adjusted to 3.00 ± 0.05 with HCl or NaOH solutions. Solution compositions are given in Table IV and the spectra in Figure 10.

Tin(IV)-Pyrocatechol Violet Solutions. The visible and ultraviolet spectra of four series of solutions, each with a different total Sn(IV) concentration, were obtained. The compositions of these solutions are given in Tables VI, VII, VIII, and IX with the corresponding spectra given in Figures 12, 13, 14, and 15. These solutions were prepared by adding the required volume of PCV solution to an aliquot of tin(IV) solution. After mixing thoroughly, enough 3.00 M NaCl was added to give a solution 1M in Cl^-. The solution was diluted to volume with distilled H_2O and the pH adjusted to 3.00 ± 0.05 with small amounts of HCl or NaOH. The dilution error was negligible. After adjusting the pH, the spectrum was obtained using a reference solution of 1M NaCl.

Results and Discussion

Computer Programs. Six computer programs are used for the analysis of the absorbance data:

1) Matrix Rank Program
2) Species Number Program
3) Corresponding Solutions Plot Program
4) Corresponding Solutions $\bar{n}$, $[L]$ Program
5) Formation Function Program
6) Pit-Mapping .

These programs constitute a generally applicable and objective method for analyzing spectrophotometric data obtained from multicomponent systems.

The matrix rank program calculates the number of components that contribute to the absorption spectrum of a multicomponent system. The only assumption involved is that Beer's law is valid for each component.

The program calculates the number of absorbing species by performing a series of row and column operations on an absorbance matrix.

The species number program determines the number of absorbing species and gives information concerning trends in species number with wavelength or solution composition. This method is based upon the rank of an absorbance matrix.

The corresponding solutions plot program calculates corresponding solution functions, E, which are used as input for program 4. This program also plots the E functions versus total ligand concentration at each metal concentration. The corresponding solutions $\bar{n}$, $[L]$ program calculates formation function data using the E functions, C_L and C_M concentrations, and the molar extinction coefficients of the ligand as input data. The formation function program calculates stability constants from the $\bar{n}$, $[L]$ data obtained in program 4.

The pit-mapping program is a general least squares curve fitting program which is valid for nonlinear as well as linear functions. This program, using absorbance readings, C_L and C_M concentrations, and pH's as input data, calculates stability constants and molar extinction coefficients for mononuclear, polynuclear, or mixed mononuclear and polynuclear complexes.

Flow charts, input requirements, program listings, and typical data sets for programs 1, 2, 3, and 4 are given in Appendices A, B, C, and D. Program 5 is published elsewhere (1). A set of input requirements for the pit-mapping program is given in Appendix E along with a program listing and a typical data set. A flow chart is given elsewhere (68).

Pyrocatechol Violet. The results of the computer analysis of the spectra obtained from the solutions given in Table III indicate the presence of 4 pyrocatechol violet species over the pH range 0.42 to 8.18 (Table X). The spectra are interpreted in terms of stepwise acid dissociation with the corresponding pK values determined in the pit-mapping program being:

$$pK_1 = 0.261 \pm 0.003$$

$$pK_2 = 7.508 \pm 0.001$$

$$pK_3 = 8.332 \pm 0.003$$

Tin(IV)-Pyrocatechol Violet. The results of the computer analysis of the spectra obtained from the solutions given in Tables VI, VII, VIII, and IX indicate three tin(IV)-pyrocatechol violet complexes are formed (Tables XII, XIII, XIV, and XV; Figures 16 through 25). The mole ratio method of Yoe and Jones (9) and the method of Holme and Langmyhr (15) were used to obtain information concerning the composition of the complexes. The results, shown in Figures 28, 29, and 30, indicate the presence of 1:1, 1:2, and 2:1 metal-ligand complexes.

The pit-mapping program was used to calculate the stabilities and molar extinction coefficients of these complexes, since the method of corresponding solutions is not valid if polynuclear species are present. The values obtained are shown below and are tabulated in Table XVIII.

$$\log \beta_{11} = 7.801 \pm 0.133$$

$$\log \beta_{12} = 14.899 \pm 0.297$$

$$\log \beta_{21} = 12.922 \pm 0.342$$

The molar extinction coefficients of the tin(IV)-pyrocatechol violet complexes and the four forms of pyrocatechol violet are tabulated in Table XIX.

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VITA

3

William Duane Wakley

Candidate for the Degree of

Doctor of Philosophy

Thesis: STABILITY CONSTANTS OF TIN-PYROCATECHOL VIOLET COMPLEXES FROM COMPUTER ANALYSIS OF SPECTRAL DATA

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