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Graphical Methods for Determining the Number of Species in Solution from Spectrophotometric Data[1]

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A convenient graphical method for determining the number of (and changes in the number of) distinct absorbing species in a series of solution absorption spectra is presented. Examples are given. For two and three absorbing species, distinction is made between cases in which there are restrictions on stoichiometry, such as the condition that the kernel ion concentration is constant or the condition that the sum of the kernel and ligand concentrations is constant (Job's method), and cases in which there are no restrictions on stoichiometry. Of particular interest is the applicability of the method to systems in which the equilibrium coefficient of a complex changes with solution composition and to spectrophotometric rate studies. The principal advantages claimed for the present method are simplicity of practice and efficient use of the data in detecting systematic errors in absorbance measurements as a function of wavelength or systematic changes in the number of absorbing species, as a function of time in rate studies, or as a function of solution composition in equilibrium studies. The method is based on simple matrix theory; the practical equations derived are related to matrix equations at each step.

Introduction

The purpose of the present paper is to present methods for determining the number of absorbing species in a series of solutions by simple graphical analysis of absorbance data—electronic, vibrational, etc. Such methods are extremely important, as spectrophotometry is often used to examine interactions among substances in solution where it is necessary that the number of absorbing species be accurately known, *e.g.*, in kinetic studies or in the determination of complex ion formation constants. These graphical methods provide a powerful alternative to the matrix approach (see below) to such determinations. In particular, these methods give a picture of trends in the number of absorbing species as a function of wavelength or solution composition which is often extremely helpful for the design of additional experiments. *It is especially recommended that these graphical tests be preliminary to any extensive study of a system by absorption spectroscopy.*

In the following discussion, we assume a series of solutions, numbered in some logical sequence, *e.g.*, in order of increasing concentration of some solute in an equilibrium study or in order of increasing reaction time in a kinetic study, and that an absorbance spectrum of each solution has been taken over the widest practical range of wavelengths. The absorbance value of a particular solution j at a specific wavelength i is denoted A_{ij}; *e.g.*, the absorbance of solution 2 at wavelength 3 is denoted A_{32}; the entire set of absorbance data is displayed as the matrix $||A_{ij}||$. In the graphical techniques to be presented, various functions of these absorbances, related to the rank of $||A_{ij}||$, are plotted to produce linear displays.

Several authors[4-9] have pointed out that the rank of $||A_{ij}||$ may be interpreted as being equal to the number of absorbing species. Although the determination of the rank of $||A_{ij}||$ requires careful consideration of propagation of errors, Wallace and Katz[7] and Varga and Veatch[9] have developed procedures suitable for handling experimental uncertainties based on the null hypothesis (*i.e.*, excluding systematic errors), and Katakis[8] has claimed a method for detecting systematic errors in original data. However, while these methods all require sophisticated computer analyses, they give as a result only the rank of the entire absorbance matrix considered. On the other hand, the present graphical methods, while relying on the same numerical relationships which determine the rank of $||A_{ij}||$, give a picture of the changes in the rank of $||A_{ij}||$ (if any) as a function of wavelength or solution composition, while also providing a rapid and convenient desk method of calculation.

Theory

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 the value of a determinant is zero if its rows or columns are linearly dependent, the rank of a matrix gives the number of *linearly independent* elements of the matrix; for an absorbance matrix this is the number of absorbing species in solution. If the matrix $||A_{ij}||$ is of rank R, where R is the number of independent absorbing species, then each determinant $|A_{ij}|$ of order $R + 1$ must vanish. This is the condition tested.

Determination and Interpretation of $|A_{ij}| = 0$. When $R = 1$, eq 1 must hold true, not only with the elements shown but also with the second column replaced by A_{13} and A_{23}, by A_{14} and A_{24}, or by the absorbances at these two wavelengths from any other solution composition in the series.

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

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.
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(4) J. C. Sternberg, H. S. Stille, and R. H. Schwendeman, *Anal. Chem.*, **32**, 84 (1960).
(5) R. M. Wallace, *J. Phys. Chem.*, **64**, 899 (1960).
(6) S. Ainsworth, *ibid.*, **65**, 1968 (1961).
(7) R. M. Wallace and S. M. Katz, *ibid.*, **68**, 3890 (1964).
(8) D. Katakis, *Anal. Chem.*, **37**, 876 (1965).
(9) L. P. Varga and F. C. Veatch, *ibid.*, **39**, 1101 (1967).

Equation 1 may be interpreted as a series of points with (x, y) coordinates (A_{11}, A_{21}), (A_{12}, A_{22}), and, generally, (A_{1j}, A_{2j}). The determinant requires that these (x, y) points fall on a straight line passing through the origin.[10] In other words, when the absorbance at one wavelength is plotted *vs.* the absorbance at each other wavelength, a set of lines radiating from the origin is obtained when the absorption in the series of spectra is caused by a single species.

When $R = 2$, each 3×3 determinant must vanish. For graphical display, it is useful to consider eq 2, in which each column is divided by its first element.

$$\begin{vmatrix} 1 & 1 & 1 \\ A_{21}/A_{11} & A_{22}/A_{12} & A_{23}/A_{13} \\ A_{31}/A_{11} & A_{32}/A_{12} & A_{33}/A_{13} \end{vmatrix} = 0 \qquad (2)$$

This equation restricts the three points with (x, y) coordinates $(A_{21}/A_{11}, A_{31}/A_{11})$, $(A_{22}/A_{12}, A_{32}/A_{12})$, and $(A_{23}/A_{13}, A_{33}/A_{13})$ to a single straight line. The same line will also contain points $(A_{2j}/A_{1j}, A_{3j}/A_{1j})$ arising from other solution compositions. Thus, 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 absorbing species.

When $R = 3$, each 4×4 determinant must vanish. We reduce this to a form suitable for graphical display starting with eq 3. A third-order determinant results

$$\begin{vmatrix} 1 & 1 & 1 & 1 \\ A_{21}/A_{11} & A_{22}/A_{12} & A_{23}/A_{13} & A_{24}/A_{14} \\ A_{31}/A_{11} & A_{32}/A_{12} & A_{33}/A_{13} & A_{34}/A_{14} \\ A_{41}/A_{11} & A_{42}/A_{12} & A_{43}/A_{13} & A_{44}/A_{14} \end{vmatrix} = 0 \qquad (3)$$

from subtracting the first column from each of the other columns and then expanding along the first row (which now contains three zeros). Dividing each row of the third-order determinant by its last element, we obtain

$$\begin{vmatrix} \dfrac{A_{11}A_{22} - A_{12}A_{21}}{A_{11}A_{24} - A_{14}A_{21}} \times \dfrac{A_{14}}{A_{12}} & \dfrac{A_{11}A_{23} - A_{13}A_{21}}{A_{11}A_{24} - A_{14}A_{21}} \times \dfrac{A_{14}}{A_{13}} & 1 \\ \dfrac{A_{11}A_{32} - A_{12}A_{31}}{A_{11}A_{34} - A_{14}A_{31}} \times \dfrac{A_{14}}{A_{12}} & \dfrac{A_{11}A_{33} - A_{13}A_{31}}{A_{11}A_{34} - A_{14}A_{31}} \times \dfrac{A_{14}}{A_{13}} & 1 \\ \dfrac{A_{11}A_{42} - A_{12}A_{41}}{A_{11}A_{44} - A_{14}A_{41}} \times \dfrac{A_{14}}{A_{12}} & \dfrac{A_{11}A_{43} - A_{13}A_{41}}{A_{11}A_{44} - A_{14}A_{41}} \times \dfrac{A_{14}}{A_{13}} & 1 \end{vmatrix} = 0 \qquad (4)$$

Points with (x, y) coordinates given by the first and second elements of each row, respectively, are restricted to a single straight 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 eq 5 will also give a linear plot which differs only in slope from the plot from eq 4 when the data arise from three absorbing species.

$$\begin{vmatrix} \dfrac{(A_{11}A_{22} - A_{12}A_{21})}{(A_{11}A_{24} - A_{14}A_{21})} & \dfrac{(A_{11}A_{23} - A_{13}A_{21})}{(A_{11}A_{24} - A_{14}A_{21})} & 1 \\ \dfrac{(A_{11}A_{32} - A_{12}A_{31})}{(A_{11}A_{34} - A_{14}A_{31})} & \dfrac{(A_{11}A_{33} - A_{13}A_{31})}{(A_{11}A_{34} - A_{14}A_{31})} & 1 \\ \dfrac{(A_{11}A_{42} - A_{12}A_{41})}{(A_{11}A_{44} - A_{14}A_{41})} & \dfrac{(A_{11}A_{43} - A_{13}A_{41})}{(A_{11}A_{44} - A_{14}A_{41})} & 1 \end{vmatrix} = 0 \qquad (5)$$

Cases with No Restrictions on Stoichiometry.—For the case of one chemical species absorbing light over the wavelength range under study, the typical Lambert–Beer law test (which should yield a straight line through the origin when the absorbance at one wavelength is plotted for various concentrations of the absorbing species) is replaced by plotting the absorbance of a solution at one wavelength *vs.* the absorbance at one or more other wavelengths in the same solution. Absorbance data for a series of solutions of arbitrary concentration will yield a separate plot for each pair of wavelengths considered. A set of straight lines *passing through the origin* is obtained when the data are from a single species.

(At this point it should be mentioned that, as with all other analytical spectrophotometric methods, these graphical tests are perturbed by systems in which absorbances deviate from the Lambert–Beer law. There are two common causes for such deviations: (1) a solute concentration exceeding some solvating limit of the solvent or (2) association by dimerization, charge-transfer complex formation, etc. In the latter cases, further graphical tests considering additional absorbing species can often aid in determining the presence of such association and, by applying appropriate stoichiometric restrictions to the analysis, may even reveal the nature of the aggregate.)

Two absorbing species are indicated when a family of straight lines is obtained by plotting absorbance ratios at various combinations of three wavelengths according to eq 2. (If only one absorbing species is actually present, all x values in eq 2 will obviously be the same, as will all y values, regardless of solution number, yielding only a single x, y point.) Three absorbing species are indicated when a family of straight lines is obtained by plotting ratios of absorbances at four wavelengths according to eq 5.

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 chosen to maximize the absorbance changes: (a) for one species, values of A_{mj} *vs.* A_{ij}, $i \neq m$, are plotted, where m is a wavelength of maximum absorbance; (b) for two species, values of A_{mj}/A_{nj} *vs.* A_{ij}/A_{nj}, $i \neq m$ or n, are plotted, where m is defined as above and n is any other single wavelength; (c) for three species, values of $(A_{mx}A_{iy} - A_{my}A_{ix})/(A_{mx}A_{iz} - A_{mz}A_{ix})$ *vs.* $(A_{mx}A_{ij} - A_{mj}A_{ix})/(A_{mx}A_{iz} - A_{mz}A_{ix})$, $i \neq m$, $j \neq x$, y, or z, are plotted, where m is defined as above and x, y, and z are three arbitrary (but fixed) solution compositions.

Cases with Restrictions on Stoichiometry.—When stoichiometric restrictions are placed on the composition of the series of solutions to be considered, interpretation of the absorbance data becomes much easier. Sophisticated treatments have been given by Newman and Hume,[11] and we will apply some of their

(10) L. P. Varga, J. S. Coleman, and W. D. Wakley, unpublished manuscript.

(11) L. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4571, 4576, 4581 (1957).

derivations in the following discussion. Two types of restrictions will be considered—one in which the sum of the concentrations of absorbing species is held constant (for the cases of two and three absorbing species) and one in which the sum of the reactant concentrations is held constant (Job's method).[12]

The first type of restriction is that in which the sum of the concentrations of absorbing species is held constant. Metal complexes are often examined in this fashion; the ligand concentration is varied at a constant stoichiometric concentration of the kernel ion. Consider a series of complex ions, ML_n, n = 0–N, with concentrations in the jth solution denoted by $(ML_n)_j$. Let $\Sigma_{n=0}^{N}(ML_n)_j$ equal the constant stoichiometric concentration [M]. The extinction coefficients at the wavelengths i for the species of ligand number n, ϵ_{in}, depend on the wavelength but are assumed here to be independent of solution composition. The absorbance A_{ij} for the general case of N absorbing species is given by eq 6, in which t

$$A_{ij} = t[\epsilon_{i0}(M)_j + \epsilon_{i1}(ML)_j t + \ldots + \epsilon_{iN}(ML_N)_j] \quad (6)$$

is the cell path length. One of the species concentrations, say $(M)_j$, may be expressed in terms of [M] and the remaining species concentrations. The sum can now be shortened by one term. We choose one solution, j', as a reference solution and form the differences $A_{ij} - A_{ij'}$

$$A_{ij} - A_{ij'} = t\{[\epsilon_{i1} - \epsilon_{i0}][(ML)_i - (ML)_{j'}] + \ldots + [\epsilon_{iN} - \epsilon_{i0}][(ML_N)_j - (ML_N)_{j'}]\} \quad (7)$$

The rank of the matrix $||(A_{ij} - A_{ij'})||$ is 1 less than that of the original matrix $||A_{ij}||$.

With only two species, the rank of the matrix $||(A_{ij} - A_{ij'})||$ is unity, and eq 7 reduces to the general form ($n \neq n'$)

$$A_{ij} - A_{ij'} = t(\epsilon_{in} - \epsilon_{in'})[(ML_n)_j - (ML_n)_{j'}] \quad (8)$$

At some other wavelength, i', for the same solution pair we have

$$\frac{A_{ij} - A_{ij'}}{A_{i'j} - A_{i'j'}} = \frac{t(\epsilon_{in} - \epsilon_{in'})[(ML_n)_j - (ML_n)_{j'}]}{t(\epsilon_{i'n} - \epsilon_{i'n'})[(ML_n)_j - (ML_n)_{j'}]} = \text{constant} \times 1 \quad (9)$$

so that

$$(A_{ij} - A_{ij'}) = \text{constant} \times (A_{i'j} - A_{i'j'}) \quad (10)$$

A plot of $A_{ij} - A_{ij'}$ at wavelength i *vs.* the corresponding difference $A_{i'j} - A_{i'j'}$ at another wavelength i' will give a straight line passing through the origin for each i'. These graphs thus correspond to the ones used for displaying eq 1 with the quantities A_{ij} replaced by $A_{ij} - A_{ij'}$.

With three species, since the rank of the matrix $||A_{ij} - A_{ij'}||$ is 2, the situation is analogous to that described for two species with nonconstant stoichiometry. With each element A_{ij} of the 3 × 3 determinant in eq 2 replaced by $A_{ij} - A_{ij'}$, plots of $(A_{2j} - A_{2j'})/(A_{1j} - A_{1j'})$ *vs.* $(A_{3j} - A_{3j'})/(A_{1j} - A_{1j'})$ should yield a straight line for each j.

(12) A. Job, *Ann. Chim.*, [10] **9**, 113 (1928).

The other type of restriction is that in which the sum of reactant concentrations is held constant (Job's method).[12] Consider a series of solutions containing the kernel ion M, the ligand L, and the complexes ML_n, n = 0–N, with extinction coefficients ϵ_{iM}, ϵ_{iL}, and ϵ_{in}, respectively. Let brackets denote stoichiometric concentrations and parentheses denote species concentrations. In this notation, the familiar equation for Job's method becomes

$$Y_{ij} = A_{ij} - \epsilon_{iM}t[M]_j - \epsilon_{iL}t[L] = t\sum_{n=0}^{N}\{\epsilon_{in} - \epsilon_{iM} - n\epsilon_{iL}\}(ML_n)_j \quad (11)$$

The salient point is that the quantities Y_{ij} may be expressed as a sum of extinction coefficients times species concentrations, but with the resulting matrix $||Y_{ij}||$ having a rank of $R - 2$. For the case of one absorbing *complex* species, the summation sign in eq 11 is not necessary, and the rank of $||Y_{ij}||$ will be unity. Plots of Y_{ij} *vs.* $Y_{i'j}$ will thus be straight lines through the origin. *This simple test should always be made in addition to the traditional Job's method plots.*

Examples

For the purposes of this study, it was found useful to explore many more possible combinations of absorbance data than was feasible by desk calculation. Therefore, a simple computer program was written to test each data set for linearity assuming one, two, and three species for either constant or nonconstant stoichiometry. The program fit the best least-squares straight line through each data set, calculated the intercept and slope of each line, gave a measure of goodness-of-fit, and plotted the appropriate functions for each case. The captions for each data set plotted below indicate those cases treated *via* the computer program. The details of this program will be published separately.[10]

One Absorbing Species.—A series of 12 solutions containing chloranilic acid (1,4-dichloro-2,5-dihydroxyquinone), from 0.08 × 10^{-4} to 0.96 × 10^{-4} M in steps of 0.08 × 10^{-4} M, have been studied spectrophotometrically by Varga and Veatch.[9] Using their absorbance matrix for 14 wavelengths (270–335 mμ, inclusive, in steps of 5 mμ) and assuming a photometric error, ΔT, of 0.5% for the Beckman DU spectrophotometer used, a rank of unity was obtained using the program of Wallace and Katz[7] when the error matrix, S_{ij}, was calculated from eq 2 of ref 9.

$$S_{ij} = 0.43429\Delta T \text{ antilog } A_{ij} \quad (12)$$

When the 12 × 14 absorbance matrix was treated by the present method, a series of 14 straight lines passing through the origin was obtained when a single absorbing species was assumed. Seven of these lines are shown in Figure 1. Linear relationships were not obtained assuming two species with nonconstant stoichiometry.

Two Absorbing Species.—Two cases in which a constant stoichiometric concentration of kernel ion was

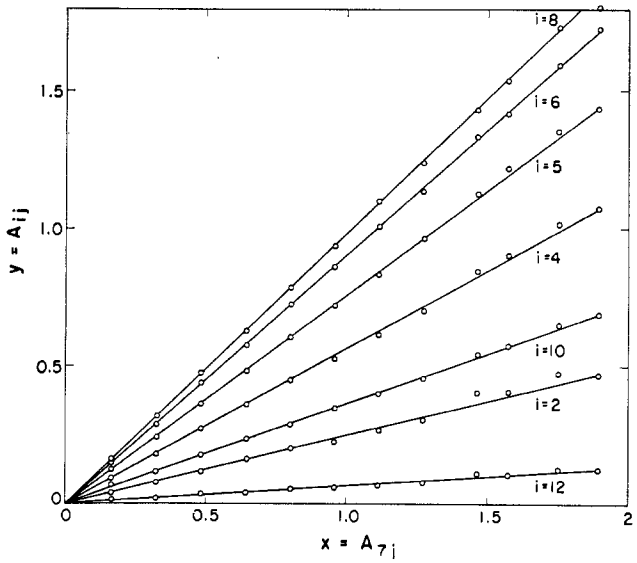

Figure 1.—A machine-assisted test for one species in the chloranilic acid system in 3 M perchloric acid. The absorbance data were taken from ref 9.

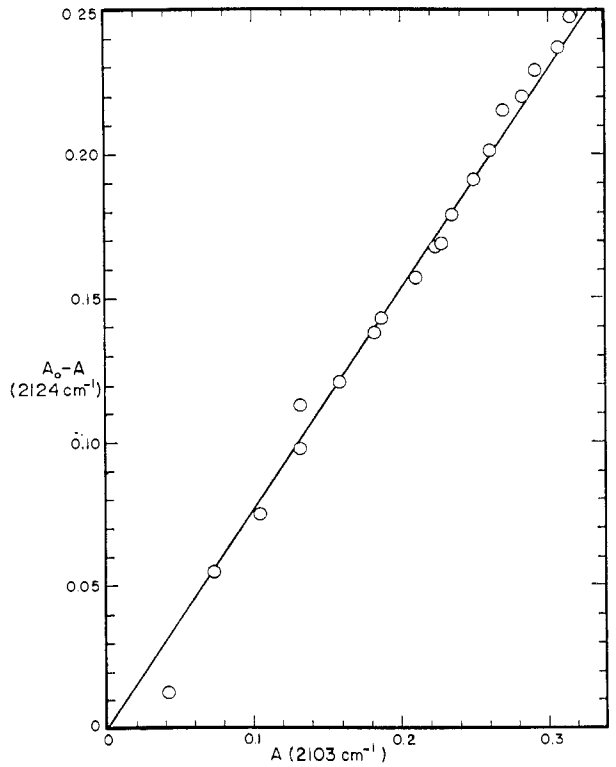

Figure 2.—A test for two species. The results are taken from ref 13. Since $A_0 > A_i$ at 2124 cm^{-1} and $A_0 = 0$ at 2103 cm^{-1}, for convenience the data are plotted as A_i (2103 cm^{-1}) *vs.* $A_0 - A_i$ (2124 cm^{-1}) as ordinate and abscissa, respectively.

present will be illustrated. In the first case, measurements of the infrared absorption at 2124 and 2103 cm^{-1} of 0.075 M $Na_2Ni(CN)_4$ containing various amounts of NaCN[13] were made for 20 solutions. These results could not be described using a single, invariant equilibrium quotient and were originally interpreted by assuming the presence of three complex species: $Ni(CN)_4^{2-}$, $Ni(CN)_5^{3-}$, and $Ni(CN)_6^{4-}$. When the present methods were applied to the data, where the solution without added NaCN was the reference solution ($\epsilon_{2103\ cm^{-1}}$ 0), the plot shown in Figure 2 was obtained. The points fall along a straight line passing through the origin, as expected from eq 10, providing powerful support for an alternative interpretation involving only two complex species, namely, $Ni(CN)_4^{2-}$ and $Ni(CN)_5^{3-}$, with a changing equilibrium quotient. These results point up a principal advantage of the present tests in such systems, namely, that no assumptions are needed regarding the invariance of the equilibrium coefficient.

Subsequent experiments by Coleman, *et al.*,[14] have confirmed the predominance of the tetra- and pentacyano complexes. These experiments provide an excellent illustration of the present graphical methods as used when more extensive data are available. Table I gives the absorbance matrix corresponding to the nickel cyanide spectra shown in Figure 3. Absorbance

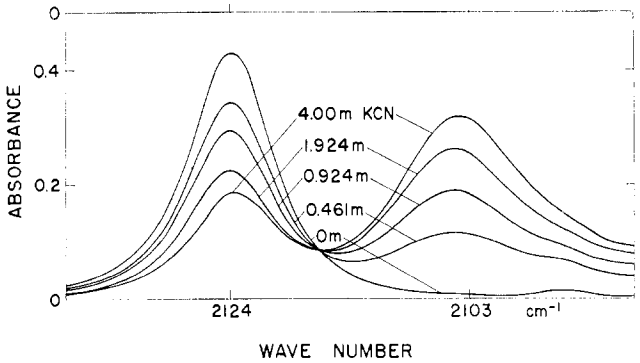

Figure 3.—Spectral curves for the nickel cyanide system. The data are from Figure 2b of ref 14.

data were obtained from these spectra at eleven wavelengths ranging from 2128 to 2078 cm^{-1} for the five solutions studied.

TABLE I
ABSORBANCE MATRIX FOR THE NICKEL CYANIDE SYSTEM,[15] [Ni(II)] = 0.075 M

		[CN⁻¹], M				
		0	0.5	1.0	2.0	4.0
		Soln. no., j				
Wavelength, i	cm^{-1}	1	2	3	4	5
		Absorbance				
1	2128	0.177	0.144	0.125	0.090	0.075
2	2123	0.425	0.340	0.289	0.220	0.183
3	2118	0.184	0.163	0.148	0.120	0.110
4	2113	0.046	0.063	0.077	0.090	0.092
5	2108	0.015	0.083	0.124	0.170	0.200
6	2103	0.007	0.114	0.187	0.261	0.317
7	2098	0.007	0.083	0.133	0.186	0.229
8	2093	0.013	0.062	0.090	0.117	0.140
9	2088	0.003	0.039	0.062	0.078	0.091
10	2083	0.004	0.037	0.055	0.068	0.084
11	2078	0.002	0.022	0.033	0.040	0.049

The rank of the matrix in Table I was found to be two using the program of Wallace and Katz,[7] assuming a photometric error of 0.3%. Graphical tests were then made for one, two, and three species, assuming a

(13) R. A. Penneman, R. Bain, G. Gilbert, L. H. Jones, R. S. Nyholm, and G. K. N. Reddy, *J. Chem. Soc.*, 2266 (1963).

(14) J. S. Coleman, H. Petersen, Jr., and R. A. Penneman, *Inorg. Chem.*, **4**, 135 (1965).

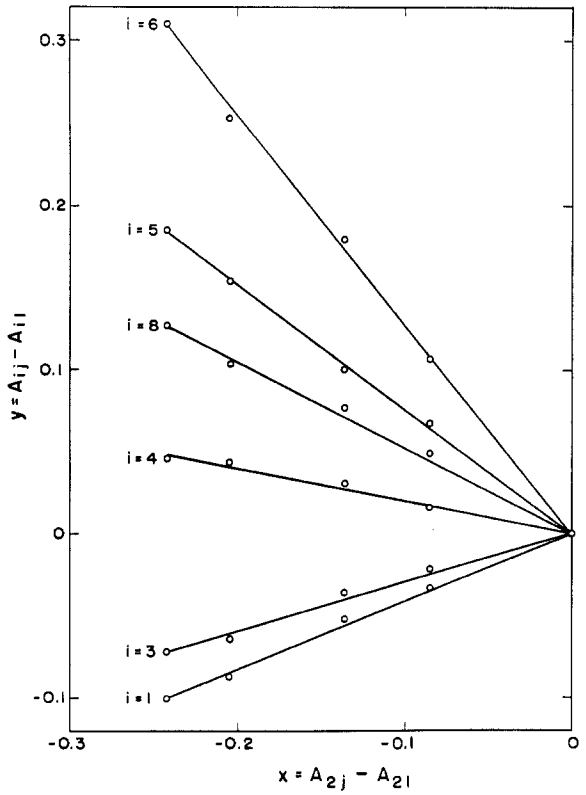

Figure 4.—A machine-assisted test for two species in the nickel cyanide system, based on the absorbance matrix of Table I.

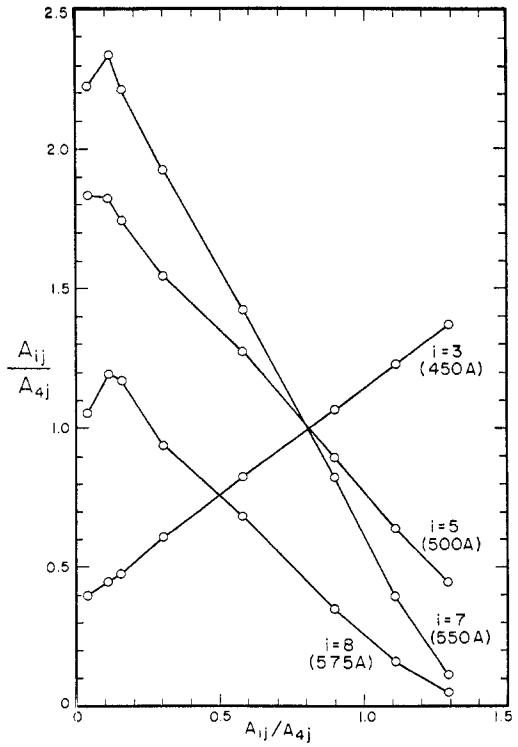

Figure 5.—Test for two methyl red species without explicit consideration of stoichiometry. The results were taken from ref 7.

constant stoichiometric kernel ion concentration in the latter two cases. The results of the test for two absorbing species, shown in Figure 4, confirm the presence of two species, six of the eleven lines actually obtained being illustrated. (It is interesting to note that the

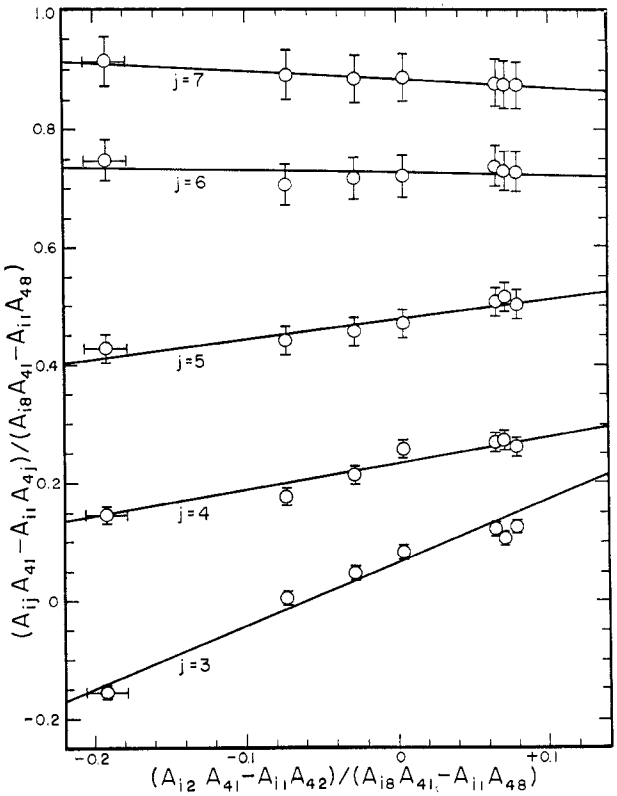

Figure 6.—Test for three methyl red species. The results were taken from ref 7. The wavelengths range from 400 to 575 mμ; the pH's of the eight solutions were about 2.2, 3.0, 3.4, 3.8, 4.6, 5.4, 6.2, and 6.6 (R. M. Wallace, private communication). The uncertainties shown correspond to an assumed uncertainty of 0.003 in the values of the individual A's.

sign of the slope changes when the wavelength range passes through an isosbestic point.) Straight lines were also obtained in the one-species test, but the lines *did not pass through the origin.*

An example of two absorbing species in a system with no restrictions on stoichiometry is given in a following section on rate studies.

Three Absorbing Species.—Spectra of methyl red were used by Wallace and Katz[7] to illustrate their matrix-rank method. For comparison, these same results will be treated here. Figure 5 illustrates the graphical test assuming two species under conditions of nonconstant stoichiometry (see eq 2). Clearly the points do not fall along a family of straight lines. Figure 6 illustrates the graphical test for three species (see eq 5). The points tend to fall along a family of straight lines, although the scatter exceeds that expected from an assumed uncertainty of 0.003 in the measured values of absorbances. The presence of at least three species was therefore indicated, but indication was given also for either the presence of a fourth species or errors exceeding 0.003. The same conclusions were reached by Wallace and Katz.[7] Note that separate curves are obtained for each solution number j instead of for each wavelength i as in the previous cases.

Rate Studies.—Spectrophotometry is often used in rate studies as a convenient means of determining concentrations of reactants and products. The utility of the present method in such studies lies mainly in the

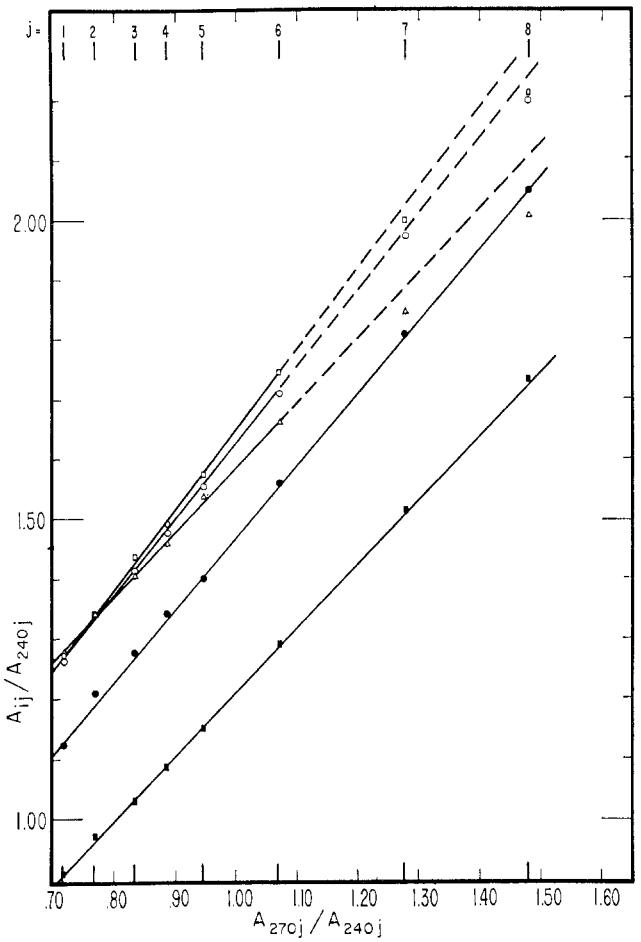

Figure 7.—Machine-assisted test for two species without explicit consideration of stoichiometry. The results were taken from ref 15, the photolysis of *cis*-$Pt(py)_2Cl_2$ in chloroform; j = 1, 2, 3, 4, 5, 6, 7, and 8 correspond to aliquots taken after 0, 5, 10, 15, 20, 31.5, 59, and 94 min of irradiation, respectively.

detection of systematic deviations in the number of absorbing species as a function of solution number, *i.e.*, as a function of time. The application of the method to such experiments is illustrated using absorbance data from the study of Mastin and Haake[15] on the mechanism of the photochemical isomerization of platinum(II) complexes.

Absorption data from the spectra of a series of aliquots taken during the photochemical isomerization of *cis*-dichlorodipyridineplatinum(II) were first plotted assuming conditions expected for a simple isomerization reaction; *i.e.*, the presence of two absorbing species with the restriction that the sum of the concentrations of the two species remains constant. The resulting plots were not linear. The same data were then plotted assuming the presence of two absorbing species with no restrictions on stoichiometry. The results, illustrated in Figure 7, do indicate the presence of two species through approximately 30 min (corresponding to solution 6), but the obvious deviations from linearity thereafter indicate that at least one other species is produced after that time. One additional fact about the third species is evident—that it absorbs strongly only at wavelengths below 265 mμ, since the plots for higher wavelengths (265 and 270 mμ) remain linear throughout the photolysis. With a bit of chemical intuition, these observations can be explained by assuming that photodecomposition (producing pyridine, which absorbs strongly below 265 mμ) occurs concurrently with photoisomerization and that photodecomposition affects mainly the *trans* isomer (since deviation from a two-species system does not become a serious problem until the concentration of the *trans* isomer becomes significant). Subsequent chemical tests suggested by the graphical analysis have confirmed these hypotheses.

The main point of this last example, however, is to illustrate the clear picture of a reaction sequence which can be obtained by the graphical method—*i.e.*, the full display of the information content of the absorbance data—as opposed to the single conclusion that there are three absorbing species in solution which would be the result of a conventional computer rank analysis.

Conclusions

The graphical methods presented provide a simple, accurate, and useful test for the number of absorbing species in a series of solutions. For systems of two or more absorbing species, the advantage is that no restrictions concerning stoichiometry need be made. In addition, there need be *no* assumptions concerning the constancy of the equilibrium coefficient of a complex with solution composition; data from systems in which such variations occur can readily be treated. The ease of application of the method to data obtained from a wide range of wavelengths and solution compositions encourages the investigator to cover such a range in his experiments. This makes it possible to eliminate the problem of having two or more species in solution with approximately equimolar absorptivities over the wavelength range studied, which can be a serious problem in Lambert–Beer law plots or in Job's method plots. Finally, the ability to detect systematic errors in absorbance measurements as a function of wavelength or changes in the number of absorbing species as a function of solution number by the graphical technique suggests strongly that these graphical tests should be employed preliminary to any extensive spectrophotometric investigation. Application to spectrophotometric data obtained from rate studies is especially indicated. These graphical methods should also find application in many other types of experiments (*e.g.*, in γ spectrometry) which are interpretable using matrix rank analysis along the lines suggested by Katakis.[8]

(15) S. H. Mastin and P. Haake, unpublished results.