KINETIC AND EQUILIBRIUM SIMULTANEOUS

ANALYSES OF SOME SULFONEPHTHALEIN

DYE MIXTURES BY THE METHOD OF

PROPORTIONAL EQUATIONS

By

GERALD LLOYD ELLIS

Bachelor of Science
Tennessee State University
Nashville, Tennessee
1958

Master of Science
Pennsylvania State University
University Park, Pennsylvania
1961

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of the Oklahoma State University
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Thesis Approved:

Horacio A Mottola
Thesis Adviser

Louis P. Varga

Tom E. Moore

H. Olin Spivey

N D Durham
Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Triphenylmethane dyes are widely used in the field of chemistry, the food and drug industries, the textile industry, and in the manufactory of inks. The phthaleins and sulfonephthleins are commonly employed as acid-base indicators. Purity tests for these indicators have been set forth by the committee on Analytical Chemistry of the American Chemical Society (58). Phenol red (phenolsulfonephthalein) has veterinary (76) and medical applications (21). Several phthalein and sulfonephthalein dyes, namely, phthalein complexone, methylthymol blue, xylenol orange, and pyrocatechol violet are noted for their uses as chromogenic agents for metal ions.

The utility of triphenylmethane basic dyes in chemical analyses is indicated by more than forty applications reported in references (6) and (7) alone. Members of this group include such dyes as, malachite green, brilliant green, methyl violet, crystal violet, ethyl violet, and pararoseaniline. Dyes of this group also have applications in medicine (74,75), in the preparation of inks (15), and in the dying of textiles (77).

Triphenylmethane acid dyes such as xylenol green A, lissamine green SF, xylene blue, and merantine blue V, are used to dye textiles (77). Five other dyes of this type have been certified by the Food and Drug Administration for use as coloring agents for food, drugs, and cosmetics

(14). These are guinea green B (FD&C green No. 1), light green SF yellowish (FD&C green No. 2), fast green FCF (FD&C green No. 3), brilliant blue FCF (FD&C blue No. 1), and acid violet 6B (FD&C violet No. 1).

Methods for preparing organic compounds such as dyes usually lack complete specificity. As a result more than one product is formed. In most instances the subsidiary products have structures and properties that are very similar to those of the primary product, making their detection and determination difficult by "in situ" procedures. Usually the presence of such impurities will interfere with the determination of the primary product itself. The presence of uncombined starting materials and reaction intermediates might also interfere with product analysis.

The literature contains numerous accounts of methods which have been used to determine the purity of various types of triphenylmethane dyes. Invariably these procedures employ a separation technique prior to determination. The techniques commonly employed are: thin-layer chromatography, paper chromatography, electrophoresis, and solvent extraction. In most instances very little information, if any at all, is reported concerning the quantitative determination after separation is achieved.

The study described in this thesis was undertaken in an effort to develop an "in situ" method for the multicomponent analysis of triphenylmethane dyes. Considering that the identity and concentrations of subsidiary components in a dye sample are not usually known, an attempt was made to develop a method which is applicable under these conditions. Accordingly, the kinetic method of proportional equations was chosen for this work. In general this method involves the simultaneous solution of

two or more non-parallel kinetic equations which relate the rate of change of an experimentally measured additive parameter of the reacting mixture to the proportionality constants and the initial concentrations of the substances being determined. Each proportionality constant is determined from reactions of a pure component and is a function of the rate constant and time. A detailed treatment of the theoretical bases, practical applications, advantages, and disadvantages of this method is given in Chapter II.

More specifically, the kinetic method employed in this work is based on the fact that under proper experimental conditions certain closely related triphenylmethane dyes are oxidized by periodate ion at significantly different rates. Low concentrations of manganese(II) ion catalyze the reaction. The rate at which a given dye is oxidized can be related to its initial concentration. Spectrophotometric measurements were used to follow the reactions. Results obtained by the kinetic method are compared with those obtained using an equilibrium spectrophotometric method. Comparable experimental techniques are used in both approaches.

Considering that the literature did not contain information relative to the kinetic determination of dye mixtures, it was decided that this study would be directed primarily toward the development of a method for the analysis of sulfonephthalein dyes. Several factors prompted this decision. First, the sulfonephthaleins are commonly used as analytical indicators. Thus, they can be obtained in a high degree of purity. Second, aqueous solutions of these dyes exhibit a greater stability than those of the acid and basic type triphenylmethanes. Third, the structures of the sulfonephthalein dyes are in general less

complex than those of other triphenylmethanes. Accordingly, one would expect their reaction mechanisms to be less complex. Fourth, the majority of sulfonephthaleins do not form complexes with metal ions as readily as the basic dyes or the phthaleins. The relevance of this factor resides in the fact that complexation of the manganese catalyst by the dyes can cause rather pronounced effects on the rates at which they are oxidized. Using these factors as intuitive guides, it was anticipated that less experimental difficulties would be encountered in the development of a method for "in situ" analysis of "simple systems", that is, mixtures of sulfonephthalein dyes. It was hoped that once a suitable method was developed for the sulfonephthaleins, the method could be modified and then applied to the analysis of mixtures of other triphenylmethanes. With this in mind some attention was given to the determination of a mixture of basic dyes.

CHAPTER II

GENERAL BACKGROUND

Kinetic Methods for the Simultaneous Analysis

of Closely Related Mixtures

In the past decade numerous accounts have been published in which kinetic methods were applied to the simultaneous "in situ" analysis of closely related species. The increasing interest in the use of kinetic approaches in Analytical Chemistry arises from the fact that it is often necessary to determine mixtures of closely related components, such as, homologs, isomers, metal ions of the same periodic group, or metal ions of neighboring periodic groups. Other factors that have contributed to the growth of analysis by kinetic methods are the development of better techniques for data aquisition and the accessibility of digital computers for data processing.

Methods based on kinetic techniques often have advantages over those based on equilibrium techniques. For example, when equilibrium procedures are employed to determine closely related species, the degree of differentiation obtained is often insufficient to resolve the individual concentrations of the components contained in the mixture. Therefore, separation of the components prior to analysis is necessary. This approach is often laborious and time consuming, making it not suitable for routine analysis of a large number of samples. In some cases, quantitative separation is impossible. In contrast, when kinetic techniques

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are applied to the analysis of these mixtures the degree of differentiation obtained is often sufficient to permit their simultaneous analysis.

Reviews of the applications of kinetic methods of analysis have been published in references (25, 26, and 59). A discussion of the basic principles, applications, and limitations of the various methods for simultaneous kinetic analysis is given below. A more detailed treatment can be found in references (40) and (41).

First-Order Logarithmic Graphical Extrapolation

The reactions of X and Y with a common reagent R under irreversible first-order or pseudo-first order conditions, i.e., $[R]_o \gg ([X]_o + [Y]_o)$ can be represented by the equations:

$$X + R \rightarrow Z \qquad\qquad (2.1)$$

$$Y + R \rightarrow Z \qquad\qquad (2.2)$$

The integrated rate equation for the reacting mixture can be written as

$$[X]_t + [Y]_t = [X]_o e^{-k_X t} + [Y]_o e^{-k_Y t} = [Z]_\infty - [Z]_t \qquad (2.3)$$

where the subscripts t and o are used to designate the concentrations of X, Y, and Z at times (t = o) and (t = t). The pseudo-first-order rate constants are represented as k_X and k_Y. If the ratio, k_X/k_Y, is sufficiently large, a time, t, will be reached at which $[X]_o e^{-k_X t}$ is relatively small compared to $[Y]_o e^{-k_Y t}$ and can be neglected. Also at this time, $[X]_t \approx 0$ while an appreciable amount of Y remains unreacted. Taking these considerations into account the logarithm of Equation (2.3) can be written

$$\ln([X]_t + [Y]_t) = \ln[Y]_0 - k_Y t = \ln([Z]_\infty - [Z]_t) \qquad (2.4)$$

A plot of either $\ln([X]_t + [Y]_t)$ or $\ln([Z]_\infty - [Z]_t)$ versus t yields a straight line having a slope, $-k_Y$, and an intercept, $\ln[Y]_0$, when extrapolated to (t = o). Beginning at the point where $[X]_t = [X]_0$ the plot will contain two straight line portions, the first arising from the reaction of X, the second from the reaction of Y. The total initial concentration of reactants, $([X]_0 + [Y]_0)$ must be determined by an independent experiment or from the value of $([Z]_\infty - [Z]_0)$. Having determined $[Y]_0$ from the intercept of the plot, the value of $[X]_0$ is calculated by difference. However, a common practice is to determine the per cent of X from the intercept and the per cent Y by difference (1,5,10,11,69,70).

A large number of applications have been reported for the first-order logarithmic graphical extrapolation method. Hydrolysis reactions (1,10,11) were used to resolve binary and ternary mixtures of alkyl chlorides. The three component mixtures gave three distinct portions in their rate plots. Siggia, et al., (69) have resolved binary and ternary mixtures of diazonium compounds. Mixtures of amides, anilides, nitriles, and (nitriles and amides) were analyzed in references (5) and (70). Differences in rates of hydrogenation have been used (68) as a basis for the determination of unsaturated acids, esters and alcohols. A method for the analysis of mixtures of oxidants is described in reference (62). Characteristic plots are shown but results from actual analysis are not reported.

Graphical extrapolation in conjunction with metal exchange reactions has been used for analysis of inorganic mixtures. Determinations for mixtures of alkaline earth ions are reported in reference (55),

mixtures of Cd and Zn in reference (35). A method for the resolution of various combinations of heavy metal ions is reported in reference (73).

Second-Order Logarithmic Graphical Extrapolation

Organic reactions frequently follow second-order kinetics. In some instances it is possible to utilize rate studies of these reactions to resolve mixtures of closely related organic compounds.

Consider the irreversible second-order reaction of a mixture, M, containing reactants, X and Y, reacting with R by the following equation

$$M + R \rightarrow Products$$
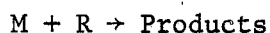
If $([X]_o + [Y]_o) \neq [R]_o$, the rate of the reaction is given by

$$\frac{dx}{dt} = k_M ([M]_o - x)([R]_o - x) \tag{2.5}$$

where $[M]_o = ([X]_o + [Y]_o)$, x is the concentration of M that has reacted at time, t, and k_M is the second-order rate constant.

Integrating Equation (2.5), taking into account that (x = o) when (t = o) and (x = x) when (t = t) yields

$$k_M t = \frac{1}{[R]_o - [M]_o} \ln\left(\frac{[R]_o - x}{[M]_o - x}\right) - K \tag{2.6}$$

If $\ln\left(\frac{[R]_o - x}{[M]_o - x}\right)$ is plotted versus t a curve having two straight-line portions results. Extrapolation of the second linear portion from a time, t, where $[X]_t \approx 0$, to the point where (t = o), i.e., the y inter-

cept, gives the value of the constant, K. Since at this intercept,

$x = [X]_o$, this point can be used to evaluate $[X]_o$ by the equation

$$\ln\left(\frac{[R]_o - [X]_o}{[M]_o - [X]_o}\right) = y \qquad (2.7)$$

The value of $[M]_o$ must be determined at $(t = \infty)$ or by an independent measurement. $[Y]_o$ is determined by difference. Alternate methods for calculating $[X]_o$ and $[Y]_o$ are given (41,53,54).

The second-order graphical extrapolation method has been applied to the determination of mixtures of primary alcohols in the presence of their secondary isomers, their closest homolog, and in the presence of a homolog further separated in the series (65). Reference (65) also describes a method that will resolve mixtures of aliphatic as well as aromatic aldehydes and ketones, mixtures of two aldehydes, and mixtures of two ketones. Consecutive homologs can be resolved by this method also.

Rates of addition of bromine to olefinic bonds were considered as a basis for the analysis of unsaturated compounds (68). Four mixtures were successfully determined using the second-order graphical method. The authors state, however, that the first-order extrapolation treatment utilizing the hydrogenation procedure seems to be more general and exhibits wider applicability than the bromination reaction.

Willeboorse and Critchfield (78) determined mixtures of primary alcohols, primary and secondary alcohols, primary and tertiary alcohols, secondary and tertiary alcohols, and one mixture containing all three types of alcohols by utilizing the reaction of the hydroxyl group with phenyl isocyanate.

Utilizing the reaction between amines and phenyl isothiocyanate, a method is presented in reference (66) for the determination of primary and secondary amines, mixtures of homologous primary and secondary amines, and mixtures of aliphatic and aromatic amines. Binary and some ternary mixtures were resolved.

An alternate method for the determination of amines is described in reference (64). The method is reported to be useful for the analysis of mixtures of primary amines, mixtures of primary amines in the presence of secondary and tertiary amines, mixtures of secondary amines, mixtures of tertiary amines, and mixtures of secondary amines in the presence of tertiary amines.

Method of Roberts and Regan

Consider a mixture, containing X and Y, reacting with R under conditions such that $([X]_o + [Y]_o) \gg [R]_o$. The reaction is pseudo-first-order with respect to R, and since the concentrations of X and Y do not change appreciably during the course of the reaction, the rate equation is

$$-\frac{d[R]}{dt} = k_X[X]_o[R] + k_Y[Y]_o[R] = K^*[R] \qquad (2.8)$$

Dividing Equation (2.8) by $[X]_o + [Y]_o$ yields

$$\frac{K^*}{[X]_o + [Y]_o} = \frac{k_X[X]}{[X]_o + [Y]_o} + \frac{k_Y[Y]_o}{[X]_o + [Y]_o} \qquad (2.9)$$

Substituting, $(1-f_X)$, for the mole fraction of Y and rearranging gives

$$f_X = \frac{[X]_o}{[X]_o + [Y]_o} = \frac{(K^* - k_Y)}{(k_X - k_Y)} \qquad (2.10)$$

The integrated form of Equation (2.8) is used to evaluate K*. Solutions of pure X and pure Y are used to measure k_X and k_Y. The value of $([X]_o + [Y]_o)$ must be obtained by an independent method. Using this information, $[X]_o$ and $[Y]_o$ can be calculated. Roberts and Regan used this method to resolve mixtures of carboxylic acids by reaction with diphenyldiazomethane (61).

The method developed by Roberts and Regan was modified (60) in order to make it more adaptable to routine analysis. Integration of Equation (2.8) yields

$$\ln([R]_t/[R]_o) = -(k_X[X]_o + k_Y[Y]_o) t = -K^* t \qquad (2.11)$$

Letting $[M]_o = ([X]_o + [Y]_o)$, substitution in Equation (2.11), followed by rearrangement gives

$$\frac{[X]_o}{[M]_o} = \frac{\ln([R]_t/[R]_o)}{t[M]_o (k_Y - k_X)} + \frac{k_Y}{(k_Y - k_X)} \qquad (2.12)$$

A plot of $\dfrac{1}{t([X]_o + [Y]_o)}$ versus $\dfrac{[X]_o}{([X]_o + [Y]_o)}$, at a predetermined constant value for the ratio, $[R]_t/[R]_o$, yields a straight line which has intercepts $1/t[Y]_o$ and $1/t[X]_o$ when the mole fraction of X equals zero and one respectively. The plot, which serves as a calibration curve, is readily constructed by evaluating the intercepts using solutions of pure X and pure Y, then drawing a line between them. In cases where the kinetics are not well behaved and the plot is not linear it still can be constructed using known mixtures of X and Y.

To insure that the optimum fractional life, $[R]_t/[R]_o$, is chosen

for measurements, Equation (2.12) is differentiated with respect to $[R]_t$ and then to t. The following is obtained (54)

$$\frac{d(df_X/d[R]_t)}{dt} = \frac{1 - Kt}{t^2 e^{-Kt}} \qquad (2.13)$$

It can be seen from this equation that the error in f_X is minimized when Kt = 1. Accordingly, from the relation $[R]_t/[R]_o = e^{-Kt}$, it can be seen that minimum error occurs when $[R]_t/[R]_o = 1/e$. It follows that t is selected to achieve this condition.

To test this method binary amines were determined by their reaction with hydroxylamine hydrochloride or semicarbazide. The reactions were followed by recording the conductance with time. Willeboordse and Meeker (79) applied the method developed by Reilley, et al., (54) to the determination of alcohols.

A modification of the Roberts and Regan method, which requires only a single measurement for an analysis, is presented in reference (38). By reaction with methyl iodide, mixtures of amines are determined. Automatic recording of the conductance as a function of time is used to follow the reactions. Resolution is achieved by use of Equation (2.11) from which the following equation can be written

$$K^* = k_X[X]_o + k_Y[Y]_o \qquad (2.14)$$

The total concentrations of reactants is determined by an independent method and can be written

$$[M]_o = [X]_o + [Y]_o \qquad (2.15)$$

By following the decrease in R with time, K^* is determined using Equa-

tion (2.11). Then $[X]_o$ is calculated by the simultaneous solution of Equations (2.14) and (2.15). $[Y]_o$ is determined by difference.

Method of Proportional Equations

When a mixture of closely related species, X and Y, reacts with reagent, R, forming products Z_X and Z_Y the reaction is pseudo-first-order with respect to X and Y if $[R] \gg ([X]_o + [Y]_o)$. Assuming that X and Y react independently when mixed, the following relation holds

$$[X]_t + [Y]_t = [X]_o e^{-k_X t} + [Y]_o e^{-k_Y t} \qquad (2.16)$$

or

$$[Z]_t = [X]_o (1 - e^{-k_X t}) + [Y]_o (1 - e^{-k_Y t}) \qquad (2.17)$$

where $[Z]_t = [Z_X]_t + [Z_Y]_t$. The value of Z, measured at two different conditions can be expressed as

$$[Z_1]_t = [X]_o K_{X1} + [Y]_o K_{Y1} \qquad (2.18)$$

$$[Z_2]_t = [X]_o K_{X2} + [Y]_o K_{Y2} \qquad (2.19)$$

Almost any experimental variable may be utilized to obtain the two conditions provided $K_{X1} K_{Y2} \neq K_{X2} K_{Y1}$. The optimum conditions, however, are those such that the ratio of K_{X1} to K_{Y1} is greater than unity at one condition but less than unity at the other.

Several papers have been published in which time is used as the variable. The longer time, t_2, is selected after taking into account the nature of the reacting system and the extent to which the reaction must

proceed in order to obtain the desired sensitivity. Having selected t_2', the optimum short time, t_{op}, is determined by an equation developed by Garmon and Reilley (20).

$$t_{op} = \frac{\ln(k_X/k_Y)}{k_X - k_Y} - \frac{\ln[(1 - e^{-k_X t_2})/(1 - e^{-k_Y t_2})]}{k_X - k_Y}. \quad (2.20)$$

Pseudo-first-order constants may also be used in Equation (2.20).

In practice the proportionality constants K_{X1}, K_{X2}, K_{Y1}, and K_{Y2} are determined from reactions of pure X and pure Y. To determine $[X]_o$ and $[Y]_o$, values of $[Z_1]_t$ and $[Z_2]_t$ are measured, then Equations (2.18) and (2.19) are solved simultaneously. Usually the value of P, a parameter proportional to Z, is measured rather than the value of Z itself.

The two time procedure has found application for the analysis of mixtures of diglycolic and glycolic acids (20), mixtures of sugars (37, 52) and mixtures of ketones (22).

When measured under two experimental conditions, the value of K^* given by Equation 16 becomes

$$K_1^* = k_{X1}[X]_o + k_{Y1}[Y]_o \quad (2.21)$$

$$K_2^* = k_{X2}[X]_o + k_{Y2}[Y]_o \quad (2.22)$$

Using these relations, Mark and Greinke (39) developed a method for the analysis of mixtures of anisaldehyde and 3-pentanone. The values of K_1^*, k_{X1}, and k_{Y1} were measured in 78% methanol-22% water while the values of K_2^*, k_{X2}, and k_{Y2} were determined in 42% methanol-58% water. K^* values for mixtures were measured under these same conditions.

Bensen and Fletcher (4) used temperature as the differentiating

variable to resolve mixtures of glycols at the 10^{-3} $\underline{M}$ to the 10^{-1} $\underline{M}$ level. Accurate results are obtained only for mixtures of ethylene glycol and butane-2,3-diol. The experimental error was about 2 to 3% for both components. It should be noted, however, that since the ratio of the proportionality constants is not reversed at the two experimental conditions this method is probably not useful when the slower reacting species is the minor component of the mixture.

The reaction of phosphate and silicate ion with Mo(VI) to form yellow heteropolymolybdates and their reduced heteropoly blues follows first-order kinetics. Employing techniques of stopped-flow spectro-photometry to make rate measurements during the first few seconds of reaction and again after 30 seconds, Ingle and Crouch (11) developed a method for the simultaneous determination of phosphate and silicate ions. After standards were run, five simultaneous determinations could be made in fifteen minutes.

The method of proportional equations has also been applied in a determination which employs the use of enzyme-catalyzed reactions (37). This method was used to determine mixtures of ethanol and 1-propanol. The results are not very accurate but the validity of the method is demonstrated. Two concentrations of the coenzyme, nicotinamide adenine dinucleotide are used to develop the proportional relations.

A method for the simultaneous determination of five organic peroxides of different classes (two peroxycarboxylic acids, two diacyl peroxides, and one hydroperoxide) has been developed by Hawk, et al. (27). The main basis for this method is the fact that each of the peroxides is reduced by sulfides at a different rate, leaving varying amounts of total peroxide unreacted at a given time.

In recent years, several papers have been published in which the simultaneous kinetic determination of n species involves the use of a number of measurements m where (m > n). Since the metal exchange reactions on which these reactions are based are extremely fast, stopped-flow spectrophotometry is employed in most of these analysis. Digital computers are used for the processing of data.

Binary and ternary mixtures of alkaline earth ions (Mg, Ca, Sr, and Ba) have been determined (55). For a number of runs graphical extrapolation was employed, yielding results comparable to those obtained by computer analysis. A linear regression analysis program was applied to (30 to 60) sets of absorbance versus time data to obtain a simultaneous solution for the unknown metal ion concentrations. Ten to 100 fold excess of other metals do not interfere with the alkaline earth determinations at the 10^{-6} $\underline{M}$ to 10^{-4} $\underline{M}$ concentration range.

Multicomponent mixtures of transition and lanthanide metals were determined (35). One example is given in which seven metals of a nine component mixture were determined with an accuracy of about 10%. A graphical treatment was used to resolve Cd to Zn ratios ranging from (1 to 10) to (10 to 1), with an average relative error of about 2% for Cd and 6% for Zn.

Employing stopped-flow spectrophotometry in conjunction with a small on-line computer, a method is described (80) for the determination of binary and ternary mixtures of alkaline earth metals. The mixtures were resolved by a linear least squares treatment of 200 data points taken at regularly spaced time intervals. In general, the precision and accuracy of the results were improved 5 to 10 times over those obtained when 30 points (55) were used under similar conditions.

Single Point Method of Lee and Kolthoff

If a mixture, X + Y, reacts irreversibly by first-order kinetics forming a common product, Z, the integrated form of the rate expression can be written

$$[Z]_\infty - [Z]_t = [X]_t + [Y]_t = [X]_o e^{-k_X t} + [Y]_o e^{-k_X t} \qquad (2.23)$$

Dividing by $([X]_o + [Y]_o)$ and rearranging yields

$$\frac{[X]_t + [Y]_t}{[X]_o + [Y]_o} = \frac{[Z]_\infty - [Z]_t}{[Z]_\infty} = \frac{[X]_o}{[X]_o + [Y]_o} (e^{-k_X t} - e^{-k_Y t}) + e^{-k_Y t}$$

$$(2.24)$$

A plot of $\dfrac{[Z]_\infty - [Z]_t}{[Z]_\infty}$ or $\dfrac{[X]_t + [Y]_t}{[X]_o + [Y]_o}$ versus $\dfrac{[X]_o}{[X]_o + [Y]_o}$ yields a

straight line show intercepts are $e^{-k_Y t}$ and $e^{-k_X t}$ when the mole fraction of X equals zero and one respectively. This plot, which serves as a calibration curve can be constructed by reactions of pure X and pure Y or from known mixtures of X and Y.

The optimum time at which measurements should be made is calculated from Equation (2.25) (32)

$$t_{op} = \frac{\ln(k_X/k_Y)}{k_X - k_Y} \qquad (2.25)$$

Kilthoff and Lee (30) applied this method to determine the per cent of internal and external double bonds in synthetic rubbers. The procedure used is based on the differences in the rates of reaction of perbenzoic acid with the two types of bonds. A method is described in

reference (18) that utilizes competing rates of oxime formation to determine aromatic aldehydes in the presence of aromatic ketones.

Employing a modification of the Lee and Kolthoff method, Papa et al., (52) developed a procedure for the determination of mixtures of sugars. By this procedure the calibration curve consisted of a plot of the fraction of reactant having reacted at time t versus the mole fraction of X. The procedure for preparing the curve are similar to those described above. The intercepts are $(1-e^{-k_Y t})$ and $(1-e^{-k_X t})$ when the mole fraction of X equals zero and one respectively.

Lohman and Mulligan (33) have applied the method of Lee and Kolthoff to the analysis of mixtures of ethanolamides. Differences in the rates of saponification of mono- and diethanol-amides are utilized to determine these amides in the presence of amines, amine soaps, amine esters, and the ester function of amide esters, all of which are commonly found in commercial alkanolamides.

Second-Order Single Point Method of Lee and Kolthoff

A single-point method designed for the analysis of mixtures of X and Y reacting by second-order kinetics was introduced by Lee and Kolthoff (14). The method is applicable only under conditions where $[R]_o = ([X]_o + [Y]_o)$. To resolve a mixture the quantities, $([X]_t + [Y]_t)$ and $([X]_o + [Y]_o)$, are measured. The value of $\%[X]_o$ is then read from a calibration, i.e., a plot of $\%([X]_t + [Y]_t)$ versus $\%[X]_o$, obtained from reactions of known mixtures of X and Y. The value of $\%[Y]_o$ is determined by difference. Mixtures of esters, olefins and carbonyl compounds were analyzed by this method (32).

Linear Extrapolation Method

This method was developed by Reilley and Papa (60) for the analysis of mixtures of X and Y reacting with reagent, R, by second-order kinetics under conditions such that $([X]_o + [Y]_o) = [R]_o$. The authors showed that after component X has reacted completely the following equation is valid:

$$x = k_Y [Y]_o ([R]_o - x)_t + [X]_o \qquad (2.26)$$

where x equals the concentration of X and Y consumed at time, t. A plot of x versus $([R]_o - x)t$ yields a straight line having an intercept of $[X]_o$. The value of $[Y]_o$ is calculated by difference. This method and the single point and double point methods described below were applied to the analysis of mixtures of 1-butanol and 2-butanol. The three methods gave comparable results (60).

Single Point Method of Reilley and Papa

Under conditions identical to those of the previous method, the substitution of $[Y]_o = [R]_o - [X]_o$ into Equation (2.26) yields an expression for $[X]_o$ (27)

$$[X]_o = \frac{[x - k_Y ([R]_o - x)t [R]_o]}{[1 - k_Y ([R]_o - x) t]} \qquad (2.27)$$

It follows that once values for k_Y and $[R]_o$ have been ascertained, a single measurement of x makes possible the calculation of $[X]_o$.

Double Point Method of Reilley and Papa

This method is also a modification of the linear extrapolation

method described above. Experimental conditions are the same for both methods. However, when the double point method is applied, x and x', the concentration of X and Y consumed at times, t and t', are measured. Both t and t' are times after which X has completely reacted. The values of x and x' are used in two equations like (2.26), whose simultaneous solution yields $[X]_0$ (60).

$$[X]_0 = \frac{[x - \frac{([R]_0 - x)t}{([R]_0 - x')t'} x']}{[1 - \frac{([R]_0 - x)t}{([R]_0 - x')t'}]} \qquad (2.28)$$

Tangent Method

This method for the determination of binary mixtures reacting by first-order kinetics is described in reference (31). It appears, however, that no experimental applications have been reported. The method is based on the measurement of the rate of concentration change after the faster reacting component has completely reacted. By measuring the slope of the total concentration versus time plot, the rate constant, k_Y, is determined. Since at this point in the reaction $[X]_t = 0$, $[Y]_t$ is readily measured. The initial concentrations of X and Y are then calculated.

Graphical Differential and Graphical Integral Methods

These methods were developed by Schmalz and Geiseler (63) for the determination of binary mixtures whose reactions follow second-order

kinetics. Resolution is achieved by evaluation of the second-order

differential rate laws and the second-order integral. The methods were

used to determine binary mixtures of olefines.

Method for Analysis of Mixtures Reacting by Fractional-Order Kinetics

A method applicable to the determination of mixtures of X and Y

reacting by apparent fractional-order kinetics was developed by Greinke

and Mark (23). The order of the reaction with respect to the slower

reacting component, n_Y, is ascertained by a series of approximations.

After the reacting of the faster reacting component is complete, Equa-

tion (2.29) can be used to determine $[Y]_o$, the initial concentration of

the slower reacting component.

$$(n-1) \; k_Y t \; = \; 1/[Y]_t^{n-1} - 1/[Y]_o^{n-1} \tag{2-29}$$

By plotting $1/[Y]_t^{n-1}$ versus time and extrapolating to $(t \approx 0)$, the value

of $[Y]_o$ is determined. In order to determine $[X]_o$ the quantity $([X]_o +$

$[Y]_o)$ must be measured. This method was applied to the analysis of

amines (23).

Method for Analysis of Mixtures Reacting by Mixed Higher Stoichiometries

Bond, et al., have described a method for analysis of mixtures in

which the reactants, X and Y, react with different stoichiometries (9).

The method was applied to the determination of mixtures of cyclotri-

methylenenitramine and cyclotetramethylenenitramine.

A Comparison of Kinetic Methods for the Simultaneous

Analysis of Closely Related Mixtures

For the purpose of comparison, the kinetic methods reviewed in the previous section can be divided into two main classes, general methods and miscellaneous methods. Because of their flexibility and adaptability to common experimental problems the general methods find greater application than the miscellaneous ones. Several applications can be found in the literature for each of the general methods whereas, usually, only one appears for the miscellaneous methods.

Four general methods have been developed for the simultaneous analysis of mixtures: the logarithmic graphical extrapolation methods (both first- and second-order), the method of Roberts and Regan, the method of proportional equations, and the single-point method for first-order reactions developed by Lee and Kolthoff. Depending on the circumstances, each of these methods has its place in kinetic analysis. Some of them are inherently more flexible than others. Therefore, it is desirable to compare the relative advantages and disadvantages of these methods. Since the miscellaneous methods have limited flexibility and accordingly very limited applicability their comparison will not be attempted.

Graphical Extrapolation Methods (GEM)

These methods were the first to be widely used for the simultaneous kinetic analysis of closely related mixtures. Consequently, they have been applied more than the other methods. They have the following advantages:

1. Since they are based on values obtained by plotting the log of the total reactant concentration versus time, a knowledge of the rate constants is not required.

2. The methods are relatively temperature independent.

3. The plotting procedures will, in most cases, minimize small errors since the "best" straight line is drawn through several points. It is found, however, that a relative error of about 2% results from the extrapolation procedure (23).

4. These methods are not restricted to constant fractional life processes. Therefore, they can be applied in some cases where synergistic effects occur (69).

5. The second-order method can be applied under conditions where it is necessary to follow the reagent concentration rather than that of the reactants.

6. The first-order method can be used for determinations of three component mixtures.

7. These methods are very practical when only a few samples are to be analyzed.

The main disadvantage of the graphical extrapolation methods is that component X must be about 99% reacted before useful data can be collected. In many cases when this requirement is met the amount of Y remaining is insufficient for an accurate analysis. Also, since the reaction of Y must be followed for some time after the reaction of X is complete, the possibility is rather large that side reactions or back reactions will interfere with the reaction rate of component Y. Another disadvantage is that in many instances numerous samples must be withdrawn from the reacting mixture and analyzed in order to collect data

for the plot. The final disadvantage is that the total initial concentration of reactants must be determined. In many cases this requires following the reaction to time infinity.

Method of Proportional Equations (MPE)

This is the most flexible of the kinetic methods for determining closely related mixtures. Even though it was developed long after the other methods, its number and variety of applications has grown much faster than the others. The method presents many advantages over the graphical extrapolation methods (GEM).

1. Generally, the time required for an analysis is much shorter when the MPE is used. Typical times for a GEM analysis are 1.5 hours (64), 40 minutes (65), 5 hours (65), and 70 minutes (69), compared to 24 minutes (20), 1.5 minutes (29), 50 minutes (52), and 2 hours (69), for a MPE analysis.

2. Only two measurements are required for an analysis by the MPE.

3. Even though a mixture reacts by complex kinetics the MPE is applicable if the proportionality constants can be determined (20).

4. The total concentration of reactants is not required.

5. A smaller ratio of rate constants is required for accurate results. One should realize, however, that the required value for k_X/k_Y changes as the value $[X]_o/[Y]_o$ changes. Greinke and Mark (24) have shown that for $[X]_o/[Y]_o = 4$, the ratio, k_X/k_Y, should be about 7 in order to achieve good resolution. A $k_X/k_Y = 4$ would suffice using the MPE.

6. The MPE is easily adapted to the determination of multicomponent mixtures (27,35,80).

7. The MPE is readily adapted to automation, making it the pre-

ferred method for analysis of fast reactions (80) and for initial rate methods.

8. The shorter time required for an analysis makes the MPE less susceptible to errors caused by side reactions.

The method of proportional equations has the following disadvantages:

1. The method is not applicable in the presence of synergistic effects.

2. Rate constants must be carefully measured.

The Method of Roberts and Regan (MRR)

The method of Roberts and Regan has the following advantages over the method of proportional equations and the graphical extrapolation methods:

1. Small ratios of k_X/k_Y can be tolerated. For example, a mixture containing 2.5% A, where k_X/k_Y = 2.2, was determined with only a 2 to 3% error (24).

2. Since $[R]_o << ([X]_o + [Y]_o)$, side reactions are minimized.

3. The MRR is useful over a larger range of $[X]_o/[Y]_o$ as long as $K_X[X]_o$ is about five per cent to the value of K^*.

4. The large concentration of reactants will increase the rate of very slow reactions, in some cases, making them useful for kinetic determinations. This could also be a disadvantage because some reactions will be made too fast.

The disadvantages in using the method of Roberts and Regan are:

1. The total initial concentration of reactants must be determined.

2. The method is restricted to binary determinations.

3. The method can be used only when it is possible to follow the
concentration of the reagent, R, or the common product, Z.

First-Order Single-Point Method

This method, like the method of proportional equations is based on
the constant fractional life principle. Its main advantage is that by
using empirical calibration curves the method is applicable to nearly any
reaction mechanism.

The disadvantages of this method are:

1. A rate constant ratio of 4 to 1 or larger is required (32).

2. The total initial concentration of reactants must be determined.

3. The method is limited to binary determinations.

<div align="center">

Spectrophotometric Equilibrium Methods

for the Simultaneous Analysis

of Closely Related Mistures

</div>

The principles of equilibrium absorptiometric methods are well
established. Extensive and comprehensive treatments of the methodology
associated with spectrophotometry are presented by Mellon (44), Stearns
(71,72), Lothian (34), Meehan (42), and Calder (13). Techniques employed
for multicomponent "in situ" analysis are treated in these works. In
addition to these monographs a critical survey of the instrumentation and
applications of Light Absorption Spectrometry during the years 1930 to
1944 was published in 1945 (43). Subsequent to this survey 14 reviews
have chronicled the progress in this field of analytical chemistry
(8,45,46). These reviews document developments in this discipline from
1944 through November 1971 and include numerous applications for multi-

component analysis.

In most instances the concentration of multicomponent mixtures is resolved by the simultaneous solution of j equations of the type

$$A_{\lambda i} = \varepsilon_{1\lambda i}bC_1 + \varepsilon_{2\lambda i}bC_2 + \ldots + \varepsilon_{j\lambda i}bC_j \qquad (2.30)$$

where $i = (1 \text{ to } j)$.

In Equation (2.30), $A_{\lambda i}$ is the absorbance of the mixture at wavelength i; ε_1 to ε_j, the molar absorptivities of the absorbing components, measured at the same wavelength as A; C_1 to C_j, the molar concentrations of the components being determined; and b, the path length of the spectrophotometric cell.

A notable exception to the general procedure is one described by Przybylski (56) in which the number of analytical wavelengths is several times the number of components being determined. This technique was applied to the determination of hydrocarbon mixtures (57). The accuracy and precision of results were increased by a factor of two compared to that obtained using the general procedure in which the number of analytical wavelengths is the same as the number of species being determined.

CHAPTER III

EXPERIMENTAL METHODS AND PROCEDURES

Apparatus

Absorbances were measured with a Cary-14 spectrophotometer supplied with a thermostatable cell adapter (Cary Instruments) connected to a circulating water bath maintained at $25.0 \pm 0.2^{\circ}$C. Temperature control was maintained with a Lauda/Brinkmann Model K-2/R circulator. A Corning Model 7 pH meter equipped with a glass-calomel electrode pair was used for pH measurements.

Reagents and Solutions

Sulfonephthalein Dyes

All sulfonephthalein dyes except xylenol blue and thymol blue were Eastman white label sodium salts. The purity of these salts was checked by a modification of the paper chromatographic procedure reported by Franglen (19). Using a solvent mixture of purified tertiary amyl alcohol (200 ml) and concentrated ammonia solution (50 ml), TLC separations on cellulose Eastman Chromagram Sheets showed only traces of a contaminant in cresol red, cresol purple, and bromocresol green, giving a yellow spot with $R_f \sim 1$. The R_f values of the dyes were comparable to those reported by Franglen. Kinetic runs on purified (by TLC) and unpurified dyes gave exactly the same results indicating no purification

was necessary and the kinetic behavior is not affected by the traces of contaminant.

Xylenol Blue, Water Soluble

(Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.) Used as received.

Thymol Blue, Sodium Salt

(Baker Analyzed Reagent, J. T. Baker Chemical Company, Phillipsburg, New Jersey.) Used as received.

Brilliant Green

(National Aniline Division, Allied Chemical and Dye Corporation, New York, New York.) Purified by Soxhlet extraction with acetone as described by Fogg (17). To insure that the brilliant green did not contain traces of malachite green, samples of the pure dyes and their mixture were chromatographed on an Eastman Chromatogram Sheet, Type K301R (Silica Gel) Thin Layer. The eluting solvent was a (2:2:1) mixture of methyl ethyl ketone, acetic acid, and isopropyl alcohol as used by Naff and Naff (50). The pure dyes gave only single spots on the chromatogram while their mixture was clearly resolved. The ratio of R_f values, brilliant green to malachite green, was 1.1.

Fresh stock solutions were prepared after three days use.

Malachite Green Perchlorate

Prepared by Therold E. Bailey, Department of Chemistry, Oklahoma State University, from malachite green oxalate by precipitation with ex-

cess sodium perchlorate in aqueous solution. The precipitate was washed with cold water and dried over concentrated sulfuric acid in a vacuum desiccator. The product gave an elemental analysis corresponding to the formula $C_{23}H_{25}N_2ClO_4$. An ultrasonic cleaner (disintegrator) was used to facilitate quick and complete dissolution of malachite green perchlorate in water. Fresh stock solutions were prepared after three days use.

Malachite Green Hydrochloride

(Allied Chemical Corporation, Morristown, New Jersey.) Used as received.

Malachite Green Oxalate

(Eastman white label.) Used as received.

Distilled Water

The water used to make solutions was purified by distilling de-ionized water in a borosilicate still equipped with a quartz immersion heater. Plain distilled water is satisfactory. Plain deionized water, however, was found to contain small amounts of organic matter which in-interfered with some of the determinations.

Other Reagents

All other reagents were Analytical Reagent grade chemicals.

Hydrochloric Acid - Potassium Chloride Buffer Solution for pH 1.20

The quantities, 335 ml of 0.5 $\underline{M}$ HCl plus 125 ml of 0.5 $\underline{M}$ KCl, were diluted to 500 ml with distilled water. Ten (10.0) ml of this buffer

were used per 25 ml of solution to be tested.

Acetate – Phosphate Buffer Solution for pH 3.50

The quantities, 70.0 g NaH_2PO_4 plus 30 ml glacial acetic acid, were diluted to 500 ml with distilled water. When necessary the pH of the resulting solution was adjusted to pH 3.50 by addition of 1.0 $\underline{M}$ NaOH or 1.0 $\underline{M}$ CH_3COOH. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Phthalate Buffer Solution for pH 4.00

The quantities, 0.5 ml of 0.1 $\underline{M}$ HCl and 5.10 g potassium hydrogen phthalate, were dissolved and diluted to 200 ml with distilled water. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Citrate – Phosphate Buffer for pH 4.00

The quantities, 6.45 g $C_6H_8O_7 \cdot H_2O$ and 10.32 g, $Na_2HPO_4 \cdot 7H_2O$, were dissolved and diluted to 200 ml with distilled water. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Acetate Buffer for pH 4.10, Ionic Strength 0.10

The quantities, 3.76 ml glacial acetic acid and 0.8032 g KOH (86.6%), were dissolved and diluted to 500 ml with distilled water. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Phthalate Buffer for pH 5.60

The quantities, 5.20 g of potassium hydrogen phthalate and 77.2 ml

of 0.25 $\underline{M}$ NaOH, were dissolved and diluted to 200 ml with distilled water.

Borate Buffer for pH 8.00

The quantities, 3.78 g H_3BO_3 and 9.8 ml of 0.25 $\underline{M}$ NaOH, were dissolved and diluted to 500 ml with distilled water. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Borate Buffer for pH 8.80

The quantities, 7.75 g H_3BO_3 and 158 ml of 0.25 $\underline{M}$ NaOH, were dissolved and diluted to 1.0 liter with distilled water. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Borate Buffer for pH 9.20

The quantities, 15.5 g H_3BO_3 and 528 ml of 0.25 $\underline{M}$ NaOH, were dissolved and diluted to 2.0 liters with distilled water. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Borate Buffer for pH 9.60

The quantities, 3.78 g H_3BO_3 and 185 ml of 0.25 $\underline{M}$ NaOH, were dissolved and diluted to 500 ml with distilled water. Ten (10.0) ml of this buffer were used per 25 ml of solution to be tested.

Procedures

General experimental procedures used in this work are described below. In order to resolve various dye mixtures the general procedures were modified. A detailed discussion of these modifications is given in

Chapter IV.

Kinetic Determination of Sulfonephthalein Dyes

After being brought to constant temperature, solution I, containing 5.00 ml of sodium periodate (0.01 $\underline{M}$) plus 10.00 ml of borate buffer (H_3BO_3-NaOH) and solution II, containing 5.00 ml of dye and 5.00 ml of the manganese (II) perchlorate solutions, were mixed by pouring back and forth between the test tubes which contained them. The change in absorbance, ΔA, of the reacting mixture was recorded over an experimentally determined time interval. The use of two-compartment reaction vessels similar to those designed by P. Dreyfus (Bolab Incorporated, Reading, Mass., Cat. No. BB568) did not offer any noticeable advantage over the test tubes except a little more freedom of operation.

Kinetic Determination of Basic Dyes

The general procedure outlined above was employed in an attempt to determine a mixture of closely related basic dyes. Initial conditions for this study were similar to those employed by Mottola (48). The actual conditions were: pH 3.50 (acetate-phosphate buffer), 0.1% periodate ion, a Mn(II) concentration of 5.0×10^{-6} $\underline{M}$, and a wavelength of 620 nm. Reaction curves for the pure dyes and their mixture are shown in Figure 8.

Spectrophotometric Determination of Sulfonephthalein Dyes

The required volumes of dye and buffer solutions were pipeted into volumetric flasks and diluted with distilled water. After thorough mixing, portions of the resulting solutions were poured directly into the spectrophotometric cell for measurements.

CHAPTER IV

RESULTS AND DISCUSSION

Kinetic Determination of Sulfonephtalein

Dye Mixtures

Sulfonephtalein dyes are slowly oxidized by periodate ion. Low concentrations of manganese(II) accelerate the process. Many other metallic ions do not catalyze the reaction appreciably. For example, at the 10^{-5} $\underline{M}$ level, none of the following exerted a detectable effect on the oxidation of phenol red in one hour's reaction time: Fe(II), Fe(III), Hg(I), Hg(II), Cu(II), Co(II), Ni(II), Cd(II), Zn(II), Pb(II), Tl(I), Ag(I), Cr(III), and La(III). For these tests the concentrations of phenol red and periodate ion were 1.0 X 10^{-5} $\underline{M}$ and 1.0 X 10^{-3} $\underline{M}$ respectively. The reactions were buffered at pH 8.00 with borate buffer.

In basic medium, pH 8 to 10, the predominate periodate species is $H_3IO_6^{2-}$ (12). Under these conditions the Mn(II) catalyzed oxidation of sulfonephthalein dyes by periodate may be represented as

$$\text{Dye} + H_3IO_6^{2-} + \text{Mn(II)} \rightarrow \text{Colorless Products} \qquad (4.1)$$
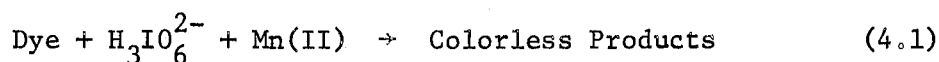
For the purpose of the work reported herein, the identities of the oxidation products were not required and therefore not determined. The rate equation for the dye oxidation is
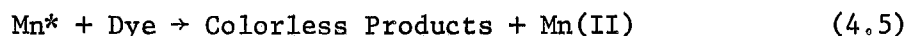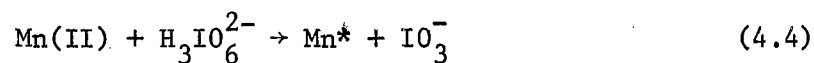
$$\frac{-d[\text{Dye}]}{dt} = k[H_3IO_6^{2-}][\text{Mn(II)}][\text{Dye}] \qquad (4.2)$$

Under the conditions employed throughout this study, i.e., $[H_3IO_6^{2-}] \gg [Dye]$, buffered reaction solutions, and a constant catalyst concentration in all "runs" of a given type, it was unnecessary to take into account the order of the oxidation reaction with respect to $[H_3IO_6^{2-}]$ and $[Mn(II)]$. Therefore, equation (4.2) could be reduced to

$$\frac{-d[Dye]}{dt} = k^*[Dye] \qquad (4.3)$$

where k^* is the pseudo-first-order rate constant. The reactions, however, were first order with respect to dye concentration. Straight lines were obtained from plots of $\log(A_t - A\infty)$ versus time (Figure 1).

The proposed reaction scheme for the reaction represented by equation (4.1) is as follows:

$$Mn(II) + H_3IO_6^{2-} \rightarrow Mn^* + IO_3^- \qquad (4.4)$$

$$Mn^* + Dye \rightarrow Colorless\ Products + Mn(II) \qquad (4.5)$$

In the above equations, Mn^* is a manganese species having an oxidation state higher than (II).

The pH dependence of the reaction is reflected by the following observations. At pH 5.6 the protonated forms of the dyes were virtually unreactive. Between pH 8.8 and 9.6 the maximum rate of oxidation was obtained while at pH 10 the rate was considerably decreased, probably due to the formation of Mn(II) hydroxide and possibly undetectable amounts of $MnO_{2(aq)}$.

Permanganate ion was not an effective oxidant under the experimental conditions at which the periodate-manganese(II) reaction provided an "in situ" generation of effective oxidizing species. Furthermore, the use of permanganate was undesirable because of its contribution to the absorbance of the reacting system. Hydrogen peroxide was found to be an ineffective oxidant and as could be anticipated, due to the high pH,
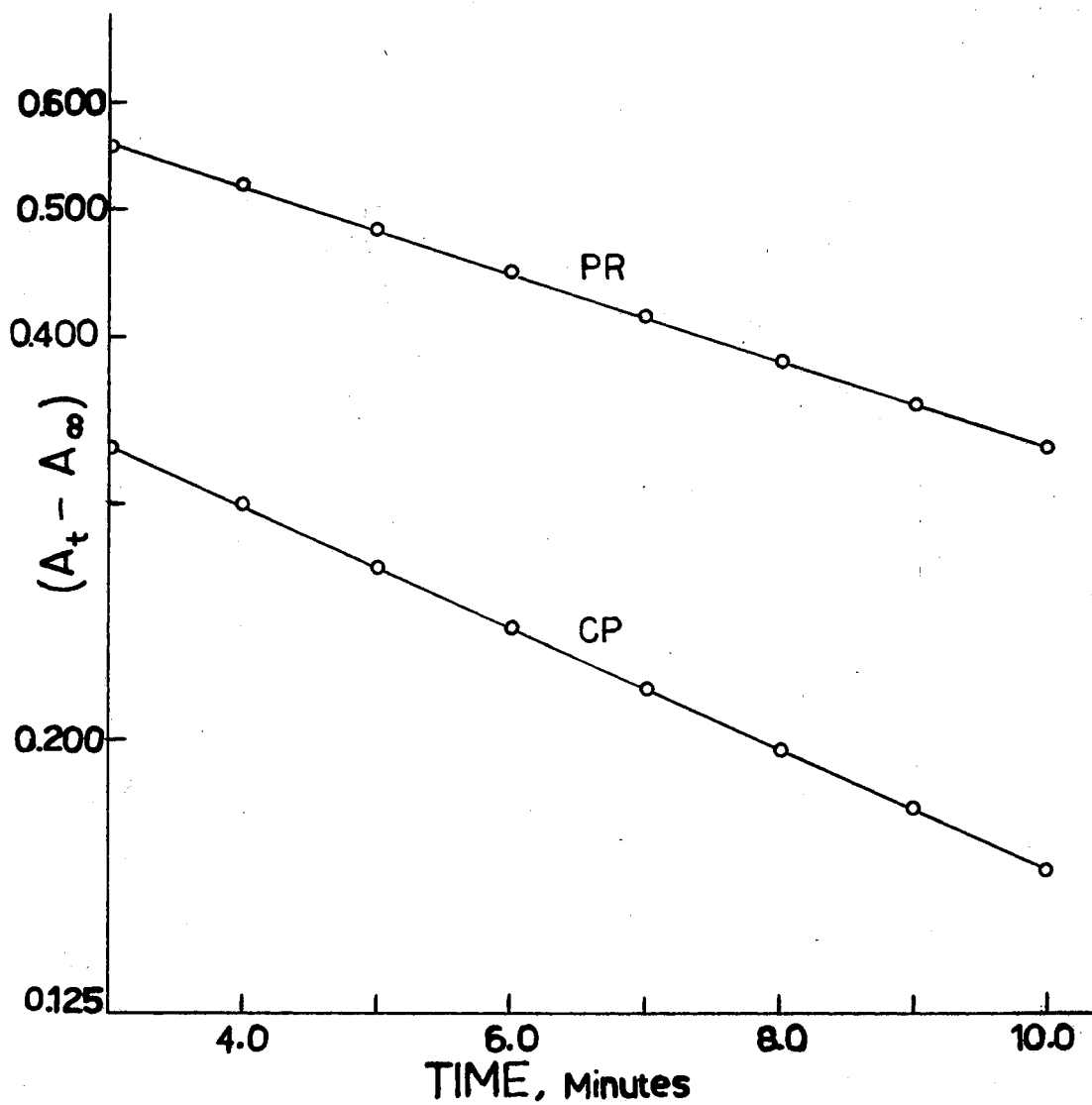
Figure 1. First-Order Rate Plots for Phenol Red and Cresol
Purple

4.0×10^{-6} M Dyes, 1.0×10^{-4} M Mn(II), 0.002 M NaIO$_4$, pH 9.20,
572 nm, 5.0 cm cells

peroxidisulfate was also ineffective. Periodate, and particularly the combination periodate-manganese(II), appeared to be a selective reagent for the oxidation of sulfonephthalein dyes within a limited range of hydrogen ion concentration. Chromate ion and cerium (IV) were not tested since even if effective the analytical procedure would be affected by hydroxide precipitation.

The effective oxidizing species, Mn*, is probably Mn(III) and the reaction proceeds according to (4.4) and (4.5) until all dye has reacted after which the periodate further oxidizes the manganese to Mn(IV) and permanganate. Aminopolycarboxylic acids such as nitrilotriacetic acid (NTA), ethylenediamine-N,N,N',N'-tetraacetic acid (EDTA), and 1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid (DCTA), all forming stronger complexes with Mn(III) than Mn(II), greatly enhance the effect of manganese. Their application to the resolution of sulfonephthalein dyes, however, is complicated by the presence of synergistic effects.

Appendix (A) illustrates the structures of the sulfonephthalein dyes included in this study. The relative reactivity of these dyes included in this study. The relative reactivity of these dyes with the periodate-manganese oxidant is demonstrated by the values of the rate constants listed in Table I. Examination of these values indicated that by proper choice of experimental conditions, the differences in reaction rates might provide a basis for quantitative "in situ" determinations of mixtures such as:

1. Cresol red and cresol purple

2. Cresol red and phenol red

3. Cresol purple and phenol red

4. Cresol red, cresol purple, and phenol red

TABLE I

KINETIC CONSTANTS

Dye	λ (nm)	pH[1]	Pseudo-First-Order Rate Constant $k^* X\ 10^2$ (min^{-1})	Experimental Proportionality Constant (3) ($K\pm s$) X 10^{-3} ($\underline{M}^{-1}$)	Time Interval (7) (Minutes)
			Section A[2]		
Bromothymol Blue	616*†	7.60	4.2		10 to 20
Bromoxylenol Blue	614*†	7.60	1.5		10 to 20
Cresol Red	572*†	9.20	0.95		0.5 to 1.5
Cresol Purple	578*†	9.20	0.12		0.5 to 1.5
Glycinecresol Red	580*†	9.20	2.1		15 to 20
Glycinethymol Blue	604*†	9.20	1.7		15 to 20
Phenol Red	558*†	9.20	0.073		0.4 to 1.5
Thymol Blue	593*†	9.20	0.63		5 to 10
Xylenol Blue	596*†	9.20	7.5		5 to 10
			Section B[4]		
Bromocresol Purple	572	9.20	0.32	0.15[5]	0.5 to 1.5
Cresol Red	572*†	9.20	16.4	24.4 ± 0.3	0.47 to 1.0
Cresol Purple	572	9.20	0.83	0.60[5]	0.47 to 1.0
Phenol Red	572	9.20	0.25	0.50[5]	0.47 to 1.0
Cresol Red	558	9.20			

TABLE I (Continued)

Dye	λ (nm)	pH[1]	Pseudo-First-Order Rate Constant $k^* \times 10^2$ (min^{-1})	Experimental Proportionality Constant (3) (K±s) X 10^{-3} ($\underline{M}^{-1}$)	Time Interval (7) (Minutes)
Cresol Purple	558	9.20			
Phenol Red	558	9.20			
			Section C[6]		
Bromocresol Green	572	9.20	0.042		1 to 10
Bromophenol Blue	590*†	8.80	0.25		0.5 to 1.5
Cresol Red	572*†	9.20	22.3	0.30[5]	6 to 8
Cresol Purple	572	9.20	10.4	10.2 ± 0.1	6 to 8
Phenol Red	572	9.20	8.1	14.0 ± 0.1	6 to 8
			Section D[6]		
Chlorophenol Red	558	8.80	1.0	6.0[5]	6 to 8
Cresol Red	558	8.80	54	0.95 ± 0.06	6 to 8
Cresol Purple	558	8.80	12.3	7.7 ± 0.0	6 to 8
Phenol Red	558*†	8.80	10.4	26.0 ± 0.4	6 to 8
			Section E[6]		
Bromocresol Purple	600	9.20	2.9	28[5]	6 to 8
Cresol Red	600	9.20	18.3	1.00 ± 0.04	6 to 9

TABLE I (Continued)

Dye	λ (nm)	pH[1]	Pseudo-First-Order Rate Constant $k^* \times 10^2$ (min^{-1})	Experimental Proportionality Constant (3) $(K \pm s) \times 10^{-3}$ ($\underline{M}^{-1}$)	Time Interval (7) (Minutes)
Cresol Purple	600	9.20	8.3	10.2 ± 0.1	6 to 9
Phenol Red	600	9.20	3.7	0.76 ± 0.10	6 to 9

*†Wavelength of maximum absorbance.

1. Clark and Lubs Buffer Solutions.

2. Reagents: 0.001M $NaIO_4$, 1.0 x 10^{-6}M Mn(II).

3. Slope of plot, $\Delta A_{(t_1 \text{ to } t_2)}$ versus C_o (dye).

4. Reagents: 0.002M $NaIO_4$, 2.0 x 10^{-6}M Mn(II).

5. Computed by $\Delta A_{(t_1 \text{ to } t_2)}/C_o$ (dye)

6. Reagents: 0.002M $NaIO_4$, 1.0 x 10^{-4}M Mn(II).

7. Interval over which constants were measured.

s = Standard deviation, calculated by Equation (4.17).

5. Xylenol blue and thymol blue

6. Chlorophenol red, cresol red, and phenol red

In Chapter III a comparison of the most commonly used kinetic methods for analyses of mixtures shows that, when applicable, the method of proportional equations (MPE) offers several advantages over other methods. In order for a mixture to be resolved by this method, however, its components must react according to the principle of constant fractional life. That is, at any time in the reaction a constant fraction of each component must remain unreacted irrespective of its initial concentration. This condition must exist for reactions of different concentrations of the pure components as well as for reactions of their mixtures. The intermediates and products formed by the reaction of one component must not promote or inhibit the reaction of other components being determined. Synergistic effects of this kind make the (MEP) inapplicable.

Other factors which determine the applicability of the (MPE) are the ratio of rate constants, k_X^*/k_Y^*, and the initial concentration ratio, $[X]_o/[Y]_o$. Depending on the concentration ratio the lower limit for the rate constant ratio ranges from about two to four (51). The ratio of proportionality constants may be considered instead of the ratio of rate constants. The lower limit for the initial concentration of each component being determined is about four percent (51).

Under the conditions employed for this work the reactions of certain sulfonephthalein dyes could be controlled such that a modified form of the (MPE) was applicable for the determination of their mixtures. The method employed was based on the following mathematical treatment:

Consider a dye mixture, X and Y, reacting with a common reagent, R,

under virtually irreversible pseudo-first-order conditions, i.e., $[R]_o \gg$ $([X]_o + [Y]_o)$, where the subscript o refers to the concentration before reaction. Assuming that X and Y react independently when mixed, the integrated form of their rate equations can be written

$$[X]_t + [Y]_t = [X]_o e^{-k_X^* t} + [Y]_o e^{-k_Y^* t} \qquad (4.6)$$

where t is any given time of reaction. Using spectrophotometric measurements to follow the reaction and assuming that the absorbance contributions of X and Y are additive, A_{XY}, the absorbance of the mixture at any time t is

$$A_{XY} = \varepsilon_X b [X]_o e^{-k_X^* t} + \varepsilon_Y b [Y]_o e^{-k_Y^* t} \qquad (4.7)$$

In Equation (4.7) b represents the path length of the spectrophotometric cell, while ε_X and ε_Y represent the molar absorptivities of X and Y respectively. The change in absorbance, ΔA_{XY}, over a given time interval, t_1 to t_2, is given by

$$\Delta A_{XY} = \varepsilon_X b [X]_o (e^{-k_X^* t_1} - e^{-k_X^* t_2}) + \varepsilon_Y b [Y]_o (e^{-k_Y^* t_1} - e^{-k_Y^* t_2}) \qquad (4.8)$$

The change in absorbance, $\Delta A_{XY}'$, over a second time interval, t_1' to t_2', is given by

$$\Delta A_{XY}' = \varepsilon_X b [X]_o (e^{-k_X^* t_1'} - e^{-k_X^* t_2'}) + \varepsilon_Y b [Y]_o (e^{-k_Y^* t_1'} - e^{-k_Y^* t_2'}) \qquad (4.9)$$

Since t_1, t_1', t_2, and t_2' are fixed times, Equations 4.8 and 4.9 can be reduced to the proportional equations:

$$\Delta A_{XY} = K_X[X]_o + K_Y[Y]_o \qquad (4.10)$$

$$\Delta A'_{XY} = K'_X[X]_o + K'_Y[Y]_o \qquad (4.11)$$

The proportionality constants in Equations 4.10 and 4.11 are functions of the molar absorptivity, the pseudo-first-order rate constant, and the analytical time interval. It follows that the values of the proportional constants could readily be altered by changes in such experimental variables as pH, wavelength, temperature, manganese concentration, and time. By selective manipulation of these variables reaction-rate differentiation was effected for various sulfonephthalein dyes. Figures 2 and 3 illustrate the type of rate differentiation that could be obtained. Curves for these figures were obtained simply by oxidizing the dyes at different concentrations of Mn(II) ion, 2.0×10^{-6} $\underline{M}$ for Figure 2 and 1.0×10^{-4} $\underline{M}$ for Figure 3.

For the work reported herein, each constant, i.e., K_X, K'_X, K_Y, and K'_Y, was evaluated by plotting ΔA, the change in absorbance over an experimentally determined time interval, versus the concentration of pure dye. These plots yielded straight lines the slopes of which were determined by least squares fits and taken to be the values of the proportionality constants. Typical plots are shown in Figure 4. Values for the constants used in this work and the conditions under which they were measured are listed in Table I. In some instances plots of this type were used as calibration curves.

Values for the proportionality constants could have been calculated from the equation

$$K_{Dye} = \varepsilon_{Dye}b(e^{-k^*_{Dye}t_1} - e^{-k^*_{Dye}t_2}) \qquad (4.12)$$
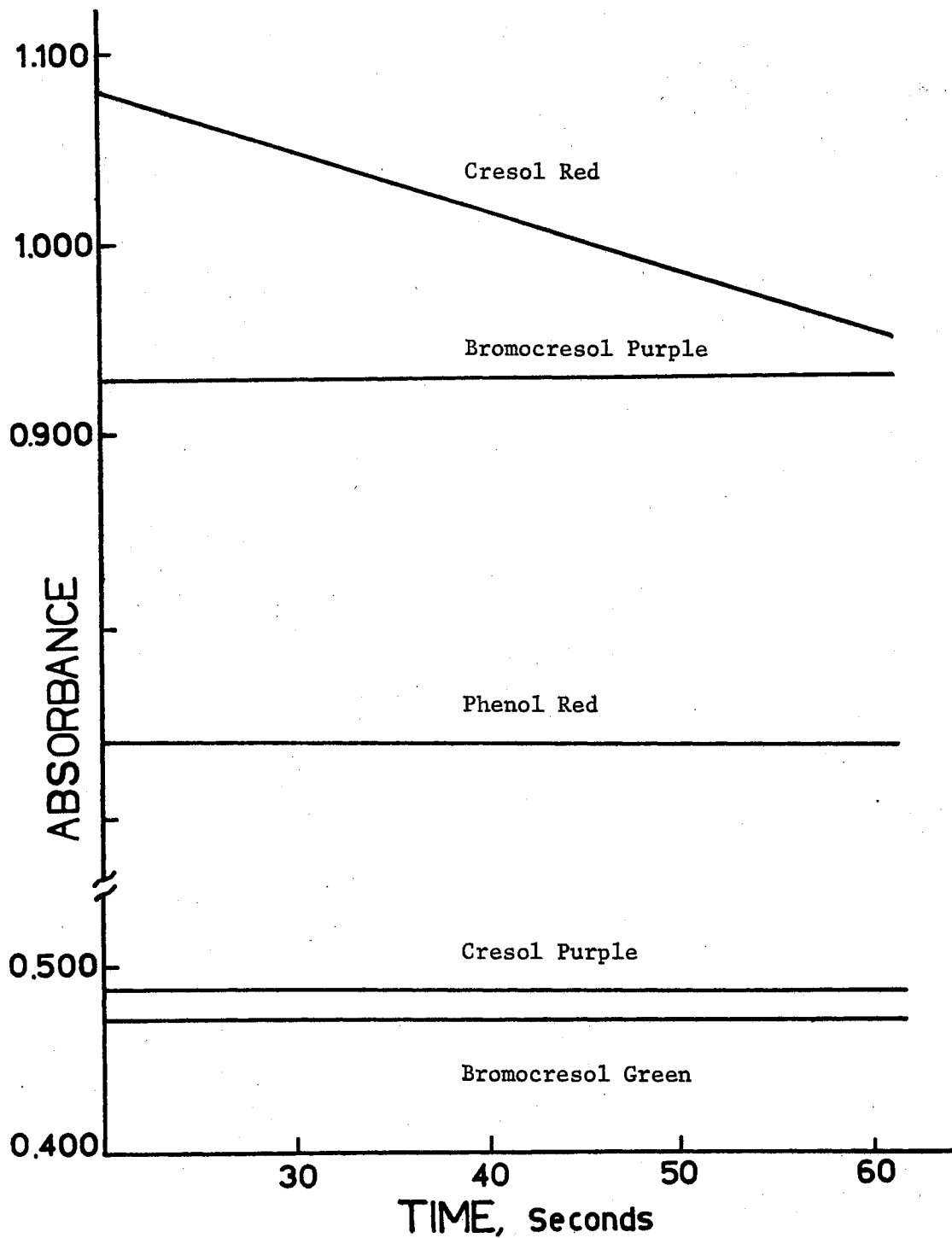
Figure 2. Absorbance Versus Time Curves for Some Sulfone-
phthalein Dyes

$2.0 \times 10^{-5}\underline{M}$ Dyes, $2.0 \times 10^{-6}\underline{M}$ Mn(II), $0.002\underline{M}$ NaIO$_4$, pH 9.20,
572 nm, 1.0 cm cells
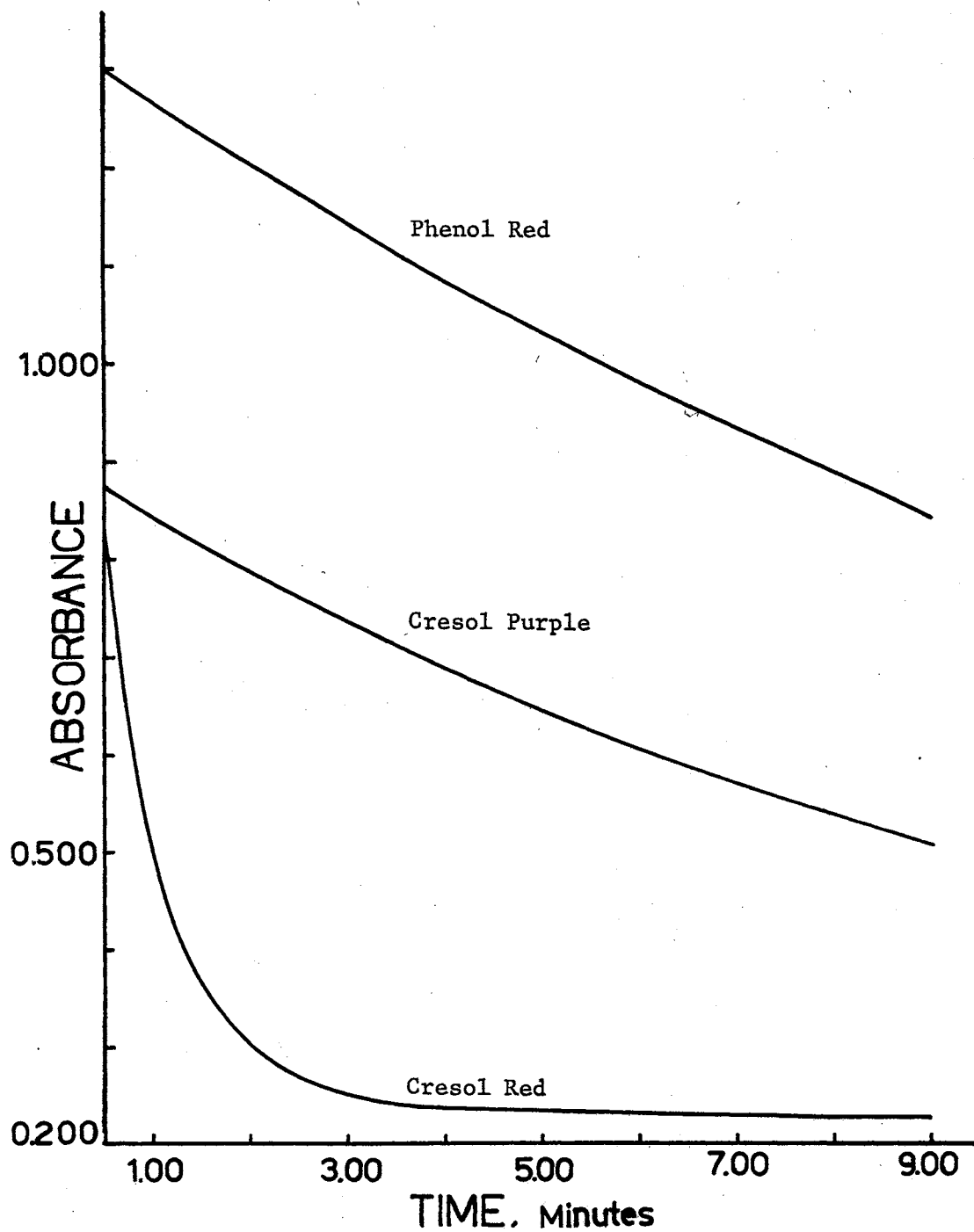
Figure 3. Absorbance Versus Time Curves for Phenol Red, Cresol
Purple, and Cresol Red

$6.0 \times 10^{-6}\underline{M}$ Dyes, $1.0 \times 10^{-4}\underline{M}$ Mn(II), $0.002\underline{M}$ NaIO$_4$, pH 9.20,
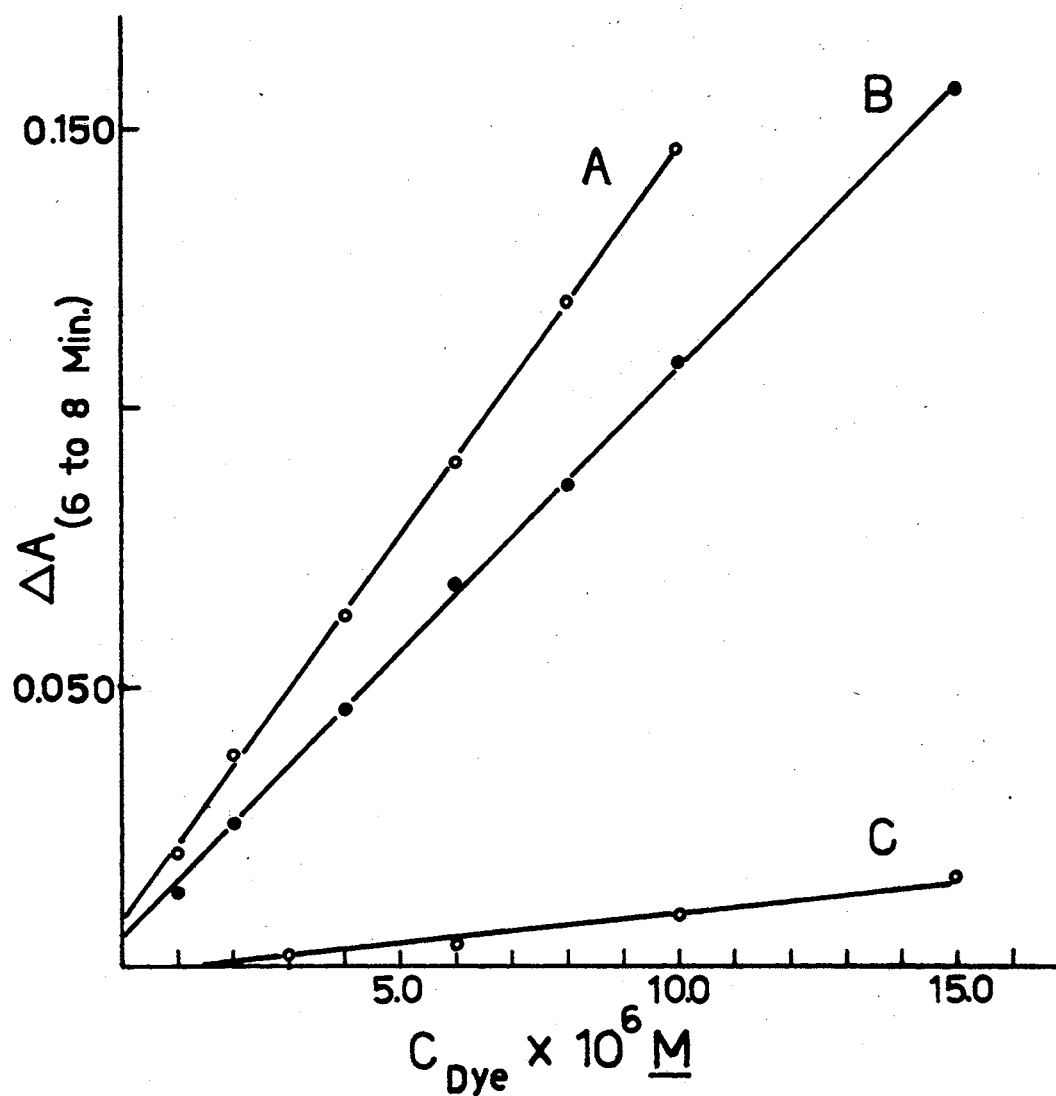572 nm, 5.0 cm cells

Figure 4. Calibration Curves for Phenol Red, Cresol Purple, and Cresol Red

A: Phenol Red, B: Cresol Purple, C: Cresol Red

$1.0 \times 10^{-4}\underline{M}$ Mn(II), $0.002\underline{M}$ $NaIO_4$, pH 9.20, 572 nm, 5.0 cm cells

However, the procedure described above was preferred since it minimizes

the influence factors unique to the reaction system. The method also

has the advantage of not requiring a knowledge of the molar absorptivi-

ties and rate constants.

In instances where the value of a proportionality constant was

needed only for purpose of comparison it was computed by use of the

equation

$$\Delta A_{Dye} = K_{Dye}[Dye]_o \qquad (4.13)$$

where ΔA_{Dye} is the change in absorbance of the pure dye measured over

the desired time interval.

Several factors were taken into account before the analytical time

intervals were selected. Since the most accurate kinetic methods of

analysis are, in general, those which utilize initial rate measurements,

the time intervals used to determine cresol red was chosen to begin as

early in the reaction as was practical, considering the time required

for mixing reactants and transferring the reacting mixture to the spec-

trophotometer for measurements. The durations of these intervals were

determined after considering to what length of time a mixture containing

cresol red plus other sulfonephthaleins could react without measurable

contributions from dyes other than cresol red (Figure 2).

Analytical time intervals for cresol purple and/or phenol red de-

terminations were selected such that if cresol red was initially present

in a mixture it would be, in most cases, completely oxidized before

$\Delta A_{Mixture}$ was measured (Figure 3). Accordingly, time intervals which

began at t = six minutes were selected. Under these conditions

$$\Delta A_{Mixture} = \Delta A_{CP} + \Delta A_{PR} \qquad (4.14)$$

where ΔA_{CP} and ΔA_{PR} represent the ΔA contributions of cresol purple and

phenol red respectively. As a result, (ΔA_{CP} and/or ΔA_{PR}) could be

measured directly, thus simpligying the determination of mixtures con-

taining cresol red plus (cresol purple and/or phenol red). The lengths

of these intervals were fixed after considering the size absorbance

change required to prevent large errors in measuring its value, the

probability of ΔA contributions from the reactions of other sulfone-

phthaleins, and the ability to obtain an additive behavior of (ΔA_{CP} +

ΔA_{PR}).

Selective Determination of Cresol Red in Sulfonephthalein Dye Mixtures

The principles for the kinetic determination of a single reacting

component of a mixture have been set forth by Garmon and Reilley (20).

For first-order or pseudo-first-order reactions with respect to dye,

the change in absorbance, ΔA, which occurs between two fixed times is

directly proportional to the initial concentration of reacting dye.

This relation may be expressed as

$$\Delta A_{Mixture} = K_{Dye}[Dye]_o \qquad (4.15)$$

Equation 4.15 characterizes the simplest case of proportional equations.

After examination of the constants listed in Table I, Section B,

and the reaction curves in Figure 2, the possibility of developing a

method for the selective determination of cresol red in the presence

of other sulfonephthaleins was pursued. Using 1.0 cm cells and a chart

speed of 5 inches per minute, photometric measurements were made at 572

nm, the wavelength at which the double charged anionic form of cresol red exhibits maximum absorbance. The change in absorbance of the reacting mixtures was recorded from 20 seconds to 1.0 minute, counting from the time at which the dye and reactants were mixed. Other experimental conditions are given in Table II.

Triplicate ΔA values were measured at each of five cresol red concentrations ranging from 5.0×10^{-6} $\underline{M}$ to 3.0×10^{-5} $\underline{M}$. A plot of ΔA versus initial cresol red concentration (Figure 5) yielded a straight line passing through the origin having a slope of $(6.2 \pm 0.2) \times 10^{3}$ l · $mole^{-1}$. This was taken to be the mean value of the proportionality constant, K_{Dye}, in Equation 4.15. Having determined the constant for the pure dye, ΔA for dye mixtures was measured. The cresol red concentration in the mixtures was then computed by use of Equation 4.15. Some experimental results are reported in Table II. Since the sulfonephthalein dyes used in this study do not interact on mixing, it was assumed that when a mixture containing cresol red and other sulfonephthaleins was oxidized any ΔA which resulted could be attributed to the reaction of cresol red (Figure 2).

Cresol Red in Multicomponent Determinations

For multicomponent determinations more accurate results were obtained when 5.0 cm rather than 1.0 cm cells were used. The increase in accuracy possibly resulted from the fact that smaller dye concentrations were reacted. Therefore, the concentration of reaction products were smaller, thus reducing the possibility that they might interfere with the reaction itself. While this effect was not particularly significant for cresol red determinations where all measurements were made within
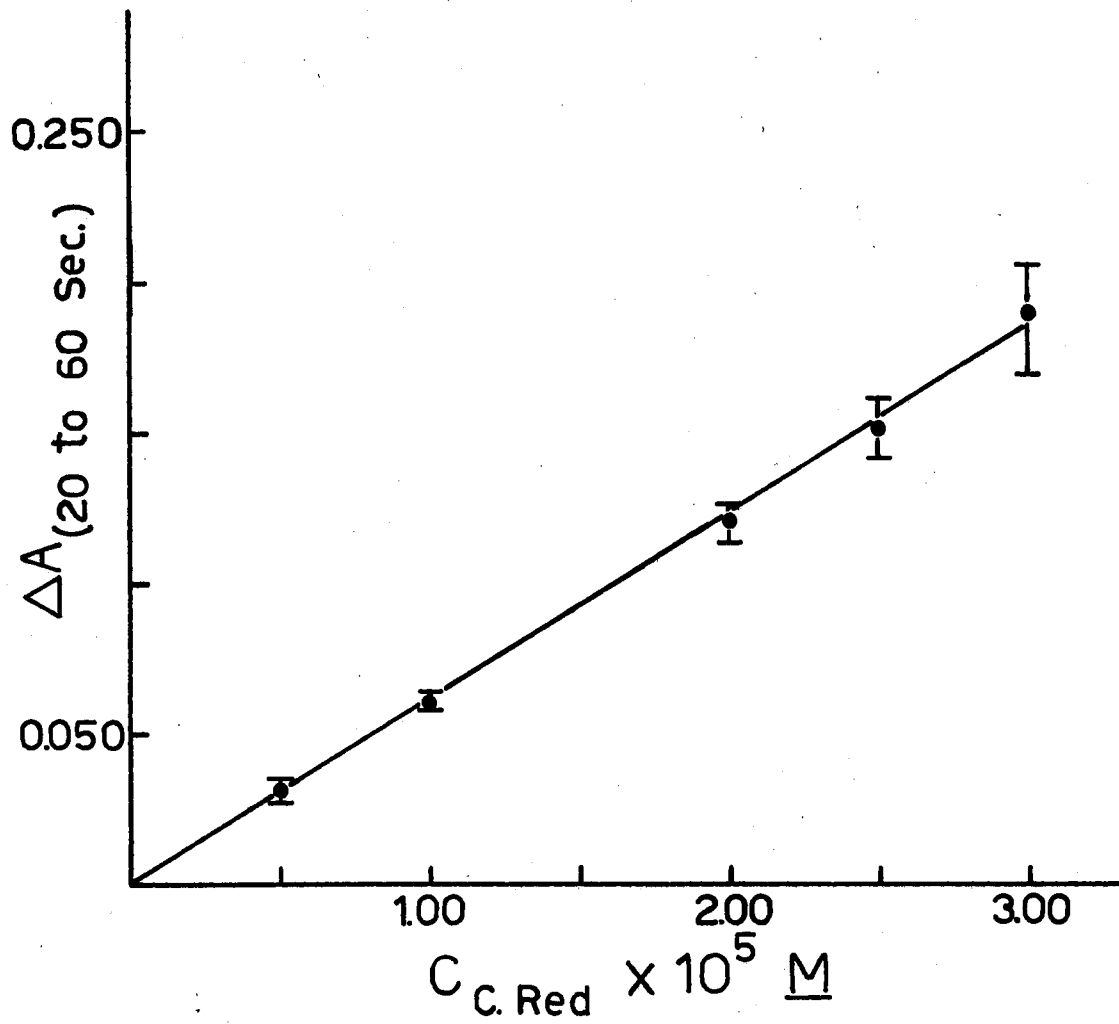
Figure 5. Calibration Curve for Cresol Red

$2.0 \times 10^{-6}\underline{M}$ Mn(II), $0.002\underline{M}$ NaIO$_4$, pH 9.20, 572 nm, 1.0 cm cells

TABLE II

KINETIC ANALYSIS OF CRESOL RED IN MIXTURES

OF OTHER SULFONEPHTHALEIN DYES

Dye	Concn in Reacting Mixture X $10^5 \underline{M}$	Results in Concn Cresol Red X $10^5 \underline{M}$	
		Found[a]	S
Cresol Red	2.50	2.50	± 0.15[b]
Cresol Purple	1.00		± 0.09[c]
Phenol Red	0.50		
Cresol Red	1.00	1.02	± 0.05[b]
Cresol Purple	1.00		± 0.05[c]
Phenol Red	1.00		
Cresol Red	0.50	0.48	± 0.03[b]
Cresol Purple	1.00		± 0.02[c]
Bromocresol Purple	1.00		
Bromocresol Green	1.00		

(a)   Mean value based on eight out of eight determinations.

S: Standard deviation

b   Based on eight replicates.
c.   Based on computation of error propagation (see page   74).

Experimental Conditions

pH = 9.20, 572 nm, 2.0 X $10^{-6}\underline{M}$ Mn(II), $0.002\underline{M}$ NaIO$_4$,

t_1 = 20 sec., t_2 = 60 sec.

the first minute of the reactions, it was significant in other determinations where measurements were not made until the sixth minute. Since more time was required to fill the larger cells, an analytical time interval of 28 to 60 seconds was used for cresol red determinations. Other experimental conditions were exactly as described in the previous section for the selective determination of cresol red.

In some runs, the cresol red reactions became significantly inhibited during the first two minutes. The cause of this inhibitory effect was traced to oxidizable ligands in the distilled, dionized water which, apparently, reduced the initial effective Mn(II) concentration. This effect was circumvented by decreasing the dye sample to 2.0 ml and increasing the manganese concentration to 4.0×10^{-6} $\underline{M}$. All components of the reaction system, except the dye itself, were mixed 10 minutes before bringing into reaction with the dye, allowing the interfering species to be destroyed by the periodate-Mn(II) oxidizing mechanism.

Simultaneous Determination of Cresol Red and Cresol Purple

Using experimental conditions listed in Table III, calibration curves, plots of ΔA_{Dye} versus $[Dye]_o$, were constructed for the two dyes (Figure 4). One portion of sample containing the mixed dyes was used to determine cresol red as described above (multicomponent determination). Having determined its concentration in the mixture, the change in absorbance of cresol red over the reaction interval six to eight minutes, $\Delta A_{(6\ to\ 8)}$, was read from its calibration curve. Using a second portion of the sample, $\Delta A_{(6\ to\ 8)}$ for the mixture was measured. The $\Delta A_{(6\ to\ 8)}$ for cresol purple was then computed from $\Delta A_{(total)} = \Delta A_{(CR)} + \Delta A_{(CP)}$. The concentration of cresol purple was subsequently read from its cali-

bration curve. Experimental results are reported in Table III.

Although $\Delta A_{(6\ to\ 8)}$ for cresol red is relatively small compared to that of cresol purple, in most instances it could not be neglected without causing significant positive errors in the results for the cresol purple concentration.

Simultaneous Determination of Cresol Red and Phenol Red

Mixtures of cresol red and phenol red were resolved using the same procedure and experimental conditions as those employed for the simultaneous determination of cresol red and cresol purple. It was found, however, that $\Delta A_{(6\ to\ 8)}$ for the dye mixtures corresponded closely to the value that would have been obtained if the sample were pure phenol red. Accordingly, a correction for ΔA_{CR} was unnecessary. Therefore, $\Delta A_{(6\ to\ 8)}$ for the mixture was taken to be ΔA_{PR}. Experimented results are given in Table IV.

Simultaneous Determination of Cresol Purple and Phenol Red

Examination of (curves C and D, Figure 2) and (curves A and B, Figure 3) showed that because of the similarities in their rates of oxidation, mixtures of cresol purple and phenol red could not be resolved under the conditions employed to determine mixtures of (cresol red and cresol purple) or (cresol red and phenol red). Therefore, the conditions were altered as follows:

Proportionality constants, K_{CP} and K_{PR}, were determined by following the reactions of pure dyes over an analytical time interval of 6 to 8 minutes at 558 nm and pH 8.80. Using a time interval of 6 to 9 minutes, constants K'_{PR} and K'_{CP} were measured at 600 nm and pH = 9.20.

TABLE III

ANALYSES OF CRESOL RED - CRESOL PURPLE MIXTURES

Mixture	Concn in Reacting Mixture $\underline{M} \times 10^5$	Spectrophotometric Results Concn* Found $\underline{M} \times 10^5$	Kinetic Results Concn* Found $\underline{M} \times 10^5$
Cresol Red	1.20	1.19	1.21
Cresol Purple	0.20	0.20	0.19
Cresol Red	0.20	0.20	0.20
Cresol Purple	1.20	1.20	1.22
Cresol Red	0.050	0.047	0.052
Cresol Purple	1.00	1.01	1.04
Cresol Red	0.40	0.40	0.39
Cresol Purple	0.40	0.39	0.40
Cresol Red	0.40	0.32	0.39
Cresol Purple	0.40	0.69	0.41
Bromocresol Green	0.20	(14% background at 572 nm; 29% at 600 nm	

*Mean value of four determinations.

Spectrophotometric Experimental Conditions

1. pH = 9.20, 572 nm
2. pH = 9.20, 600 nm

Kinetic Experimental Conditions

1. pH = 9.20, 572 nm, $4.0 \times 10^{-6} \underline{M}$ Mn(II), $0.002\underline{M}$ NaIO$_4$; t_1 = 28 sec., t_2 = 60 sec.
2. pH = 9.20, 572 nm, $1.0 \times 10^{-4}\underline{M}$ Mn(II), $0.002\underline{M}$ NaIO$_4$, t_1 = 6 min., t_2 = 8 min.

TABLE IV

ANALYSES OF CRESOL RED – PHENOL RED MIXTURES

Mixture	Concn in Reacting Mixture $\underline{M} \times 10^5$	Spectrophotometric Results Concn* Found $\underline{M} \times 10^5$	Kinetic Results Concn* Found $\underline{M} \times 10^5$
Cresol Red	0.100	0.114 ± 0.000** ± 0.012***	0.105 ± 0.006** ± 0.007***
Phenol Red	0.45	0.45 ± 0.00** ± 0.011***	0.45 ± 0.03** ± 0.02***
Cresol Red	0.45	0.45 ± 0.02** ± 0.007***	0.45 ± 0.02** ± 0.01***
Phenol Red	0.100	0.101 ± 0.004** ± 0.006***	0.103 ± 0.008** ± 0.007***
Cresol Red	0.24	0.24	0.25
Phenol Red	0.24	0.24	0.24
Cresol Red	0.18	0.19	0.18
Phenol Red	0.36	0.36	0.35
Cresol Red	0.18	0.26	0.18
Phenol Red	0.36	0.34	0.36
Bromocresol Green	0.18	(18% background at 572 nm; 10% at 588 nm)	

*Mean value of four determinations unless otherwise indicated.

**Mean and standard deviation based on eight out of eight determinations.

***Standard deviation based on computation of error propagation (see page 75).

Spectrophotometric Experimental Conditions: (1) pH = 9.20, 558 nm; (2) pH = 9.20, 572 nm.

Kinetic Experimental Conditions

1. pH = 9.20, 572 nm, $4.0 \times 10^{-6}\underline{M}$ Mn(II), $0.002\underline{M}$ $NaIO_4$, t_1 = 28 sec., t_2 = 60 sec.
2. pH = 9.20, 572 nm, $1.0 \times 10^{-4}\underline{M}$ Mn(II), $0.002\underline{M}$ $NaIO_4$, t_1 = 6 min., t_2 = 8 min.

Having measured the four constants, portions of a dye mixtures were re-
acted under each of the two conditions. The observed ΔA values and the
constants were then used to compute the concentrations by the simultane-
ous solution of equations similar to 4.10 and 4.11. Experimental results
are summarized in Table V.

Determination of Cresol Red-Cresol Purple and Phenol Red

Cresol Red is determined separately by using the procedure described
under "simultaneous determination of cresol red and cresol purple."
Cresol Purple and phenol red are simultaneously determined by the method
described above.

Cresol Red does not contribute significantly to the value of
$\Delta A_{(6 \text{ to } 8)}$ at pH = 8.8 and 558 nm. At pH = 9.2 and 600 nm, however, it
is necessary to correct for the contribution of cresol red if its concen-
tration is more than three times that of cresol purple. See Table VI
for experimental results.

Interference of Cresols and Resorcinol

Since sulfonephthalein dyes are prepared from hydroxyl derivatives
of benzene and toluene, the effect of some of these compounds on the
manganese (II) catalyzed oxidation of the dyes by periodate ion was con-
sidered. For cresol red reactions, it was found that a resorcinol to
dye ratio of 0.01 to 1.0 reduces the rate of oxidation by about 30% while
a 1 to 1 ratio stops the reaction completely. When the ratio of o-cresol
to dye is 0.01 to 1.0 the oxidation rate is reduced about 50%. The same
ratio of m-cresol to dye reduces the rate about 30%. Considering that
the dye concentration in these solutions was only $2.0 \times 10^{-6} \underline{M}$, these re-

TABLE V

ANALYSIS OF CRESOL PURPLE - PHENOL RED MIXTURES

Mixture	Concn in Reacting Mixture $\underline{M} \times 10^5$	Spectrophotometric Results Concn* Found $\underline{M} \times 10^5$	Kinetic Results Concn* Found $\underline{M} \times 10$
Cresol Purple	0.90	0.90 ± 0.01** ± 0.005***	0.90 ± 0.02** ± 0.02***
Phenol Red	0.150	0.145 ± 0.002** ± 0.002***	0.149 ± 0.005** ± 0.009***
Cresol Purple	0.150	0.148 ± 0.001** ± 0.003***	0.157 ± 0.008** ± 0.014***
Phenol Red	0.90	0.86 ± 0.01** ± 0.001***	0.87 ± 0.02** ± 0.02***
Cresol Purple	1.50	1.51	1.39
Phenol Red	0.100	0.87	0.96
Cresol Purple	0.50	0.50	0.52
Phenol Red	0.25	0.24	0.24
Cresol Purple	0.50	0.61	0.54
Phenol Red	0.25	0.29	0.24
Chlorophenol Red	0.14	(24% background at 558 nm; 21% at 600 nm)	

*Mean value of three determinations unless otherwise indicated.

**Mean and standard deviation based on eight out of eight determinations.

***Standard deviation based on computation of error propagation (see Page 75).

Spectrophotometric Experimental Conditions: (1) pH = 9.20, 558 nm; (2) pH = 9.20, 600 nm

Kinetic Experimental Conditions

1. pH = 8.80, 558 nm, 1.0 x $10^{-4}\underline{M}$ Mn(II), 0.002M NaIO$_4$, t_1 = 6 min., t_2 = 8 min.
2. pH = 9.20, 600 nm, 1.0 x $10^{-4}\underline{M}$ Mn(II), 0.002$\underline{M}$ NaIO$_4$, t_1^1 = 6 min., t_2^2 = 9 min.

TABLE VI

ANALYSES OF CRESOL RED - CRESOL PURPLE - PHENOL RED MIXTURES

Mixture	Concn in Reacting Mixture $\underline{M} \times 10^5$	Spectrophotometric Results Concn* Found $\underline{M} \times 10^5$	Kinetic Results Concn* Found $\underline{M} \times 10^5$
Cresol Red	0.80	0.84	0.81
Cresol Purple	0.20	0.18	0.22
Phenol Red	0.40	0.36	0.38
Cresol Red	0.40	0.41	0.38
Cresol Purple	0.80	0.81	0.74
Phenol Red	0.20	0.19	0.22
Cresol Red	1.60	1.63	1.63
Cresol Purple	0.20	0.18	0.18
Phenol Red	0.20	0.17	0.21
Cresol Red	0.20	0.20	0.21
Cresol Purple	1.60	1.58	1.48
Phenol Red	0.20	0.18	0.21
Cresol Red	0.16	0.17	0.17
Cresol Purple	0.32	0.31	0.32
Phenol Red	0.60	0.57	0.59

TABLE VI (Continued)

Mixture	Concn in Reacting Mixture $\underline{M} \times 10^5$	Spectrophotometric Results Concn* Found $\underline{M} \times 10^5$	Kinetic Results Concn* Found $\underline{M} \times 10^5$
Cresol Red	0.16	0.13	0.17
Cresol Purple	0.32	0.52	0.32
Phenol Red	0.60	0.55	0.60
Bromocresol Green	0.16 (2% background at 558 nm; 3% at 572 nm and 24% at 600 nm)		
Cresol Red	0.16	0.13	0.17
Cresol Purple	0.32	0.63	0.38
Phenol Red	0.60	0.53	0.59
Bromocresol Green	0.032 (6% background at 558 nm, 9% at 572 and 36% at 600 nm)		
Bromocresol Purple	0.016		
Bromophenol Blue	0.048		

*Mean value of three determinations

Spectrophotometric Experimental Conditions

1. pH = 9.20, 558 nm
2. pH = 9.20, 572 nm
3. pH = 9.20, 600 nm

Kinetic Experimental Conditions

1. pH = 8.80, 558 nm, $1.0 \times 10^{-4}\underline{M}$ Mn(II), 0.002M NaIO$_4$, t_1 = 6 min., t_2 = 8 min.
2. pH = 9.20, 572 nm, $4.0 \times 10^{-6}\underline{M}$ Mn(II), 0.002$\underline{M}$ NaIO$_4$, t_1 = 28 sec., t_2 = 60 sec.
3. pH = 9.20, 600 nm, $1.0 \times 10^{-4}\underline{M}$ Mn(II), 0.002$\underline{M}$ NaIO$_4$, t_1 = 6 min., t_2 = 9 min.

sults seem to indicate the possibility of differentiating between low concentrations of o-cresol and m-cresol.

<div align="center">
Spectrophotometric Equilibrium

Determination of Sulfone-

phthalein Dye Mixtures
</div>

An equilibrium spectrophotometric determination can be considered to be a MPE approach in which the discriminating (proportionality) constants are molar absorptivities measured at different wavelengths rather than rate constants as in a kinetic MPE. Since the kinetic MPE developed herein was to be compared with an equilibrium method which employed comparable experimental technique, the number of analytical wavelengths used in the equilibrium method was limited to the number of components being determined.

Using buffered solutions, absorption spectra of each dye; cresol red, cresol purple, and phenol red, were recorded at pH 9.20, 5.60, and 1.20. At these conditions the predominate forms of the dyes are A^{2-}, HA^-, and H_2A respectively. Examination of the spectra showed that in terms of resolution, no particular advantage was prevalent at either of the conditions. For this work, however, pH 9.20 was selected because of the high molar absorptivities of the double charged anionic forms and for the relative ase of adjusting the pH using borate buffer.

Figure 6 shows the spectra form which wavelengths were chosen for the analysis of mixtures. Wavelength selection was made such that

each of the dyes to be determined would be the primary absorbing com-
ponent at one of the analytical wavelengths. Serious wavelength errors
were minimized by selecting wavelengths in regions where changes in
absorbance with wavelength are relatively small. The choice of 600 nm,
in one case, does not adhere to this criterion. However, for this work
no serious consequences resulted in terms of conformity to Beer's law
and reproducibility of results. The wavelengths chosen are listed in
Tables III, IV, V, and VI.

Solutions of various concentrations at the 10^{-6} $\underline{M}$ level were used
to determine molar absorptivities. Duplicate, in some cases triplicate,
measurements of the absorbances of these solutions were made at each
of the analytical wavelengths. Values obtained were used to construct
plots (absorbance versus dye concentration) of the types shown in Figure
7. The values of the slopes of these plots, as determined by a least
squares fit, were divided by the path length of the cell and taken to
be the molar absorptivities of the dyes at the specified wavelength.
Values for the molar absorptivities are reported in Table VII.

The solutions whose concentrations are given in Table VIII were
used to verify the additivity of the absorbances of cresol red, cresol
purple, and phenol red when the dyes are mixed. The absorbance of each
solution listed was measured at the three chosen wavelengths. Values
obtained were compared with those computed by use of Equation (2.30).
Agreement was found to be within 1% in all cases except one where it
was about 2%.

TABLE VII

MOLAR ABSORPTIVITIES FOR SOME

SULFONEPHTHALEIN DYES

Dye	λ (nm)	Molar Absorptivity* $(\varepsilon+s) \times 10^{-4}$ $(cm^{-1} \cdot M^{-1})$
Cresol Red	572	5.83 ± 0.04
Cresol Purple	572	2.34 ± 0.01
Phenol Red	572	3.54 ± 0.08
Cresol Red	558	4.64 ± 0.02
Cresol Purple	558	2.03 ± 0.07
Phenol Red	558	5.99 ± 0.05
Cresol Red	600	1.29 ± 0.02
Cresol Purple	600	1.64 ± 0.06
Phenol Red	600	0.200 ± 0.009

*pH = 9.20, borate buffer.

s = Standard deviation, calculated from Equation (4.17).

TABLE VIII

SOLUTIONS USED TO VERIFY ADDITIVITY OF

ABSORBANCES IN DYE MIXTURES

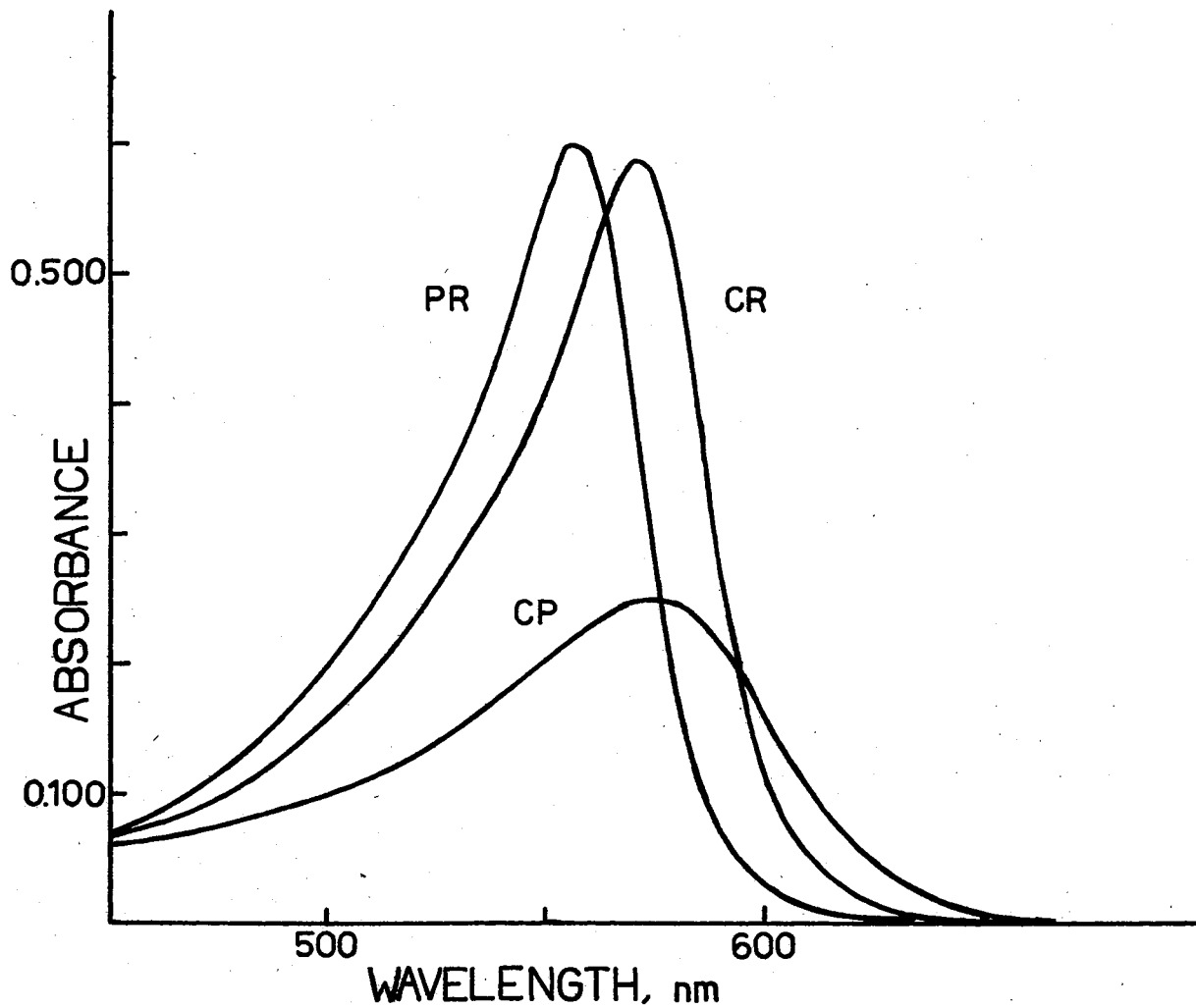| Mixture | $C_{dye} \times 10^6 \underline{M}$ | | |
	Cresol Red	Cresol Purple	Phenol Red
1	2.00	4.00	1.00
2	4.00	1.00	2.00
3	0.80	1.60	3.20

Figure 6. Aqueous Spectra of Phenol Red, Cresol Red, and Cresol Purple
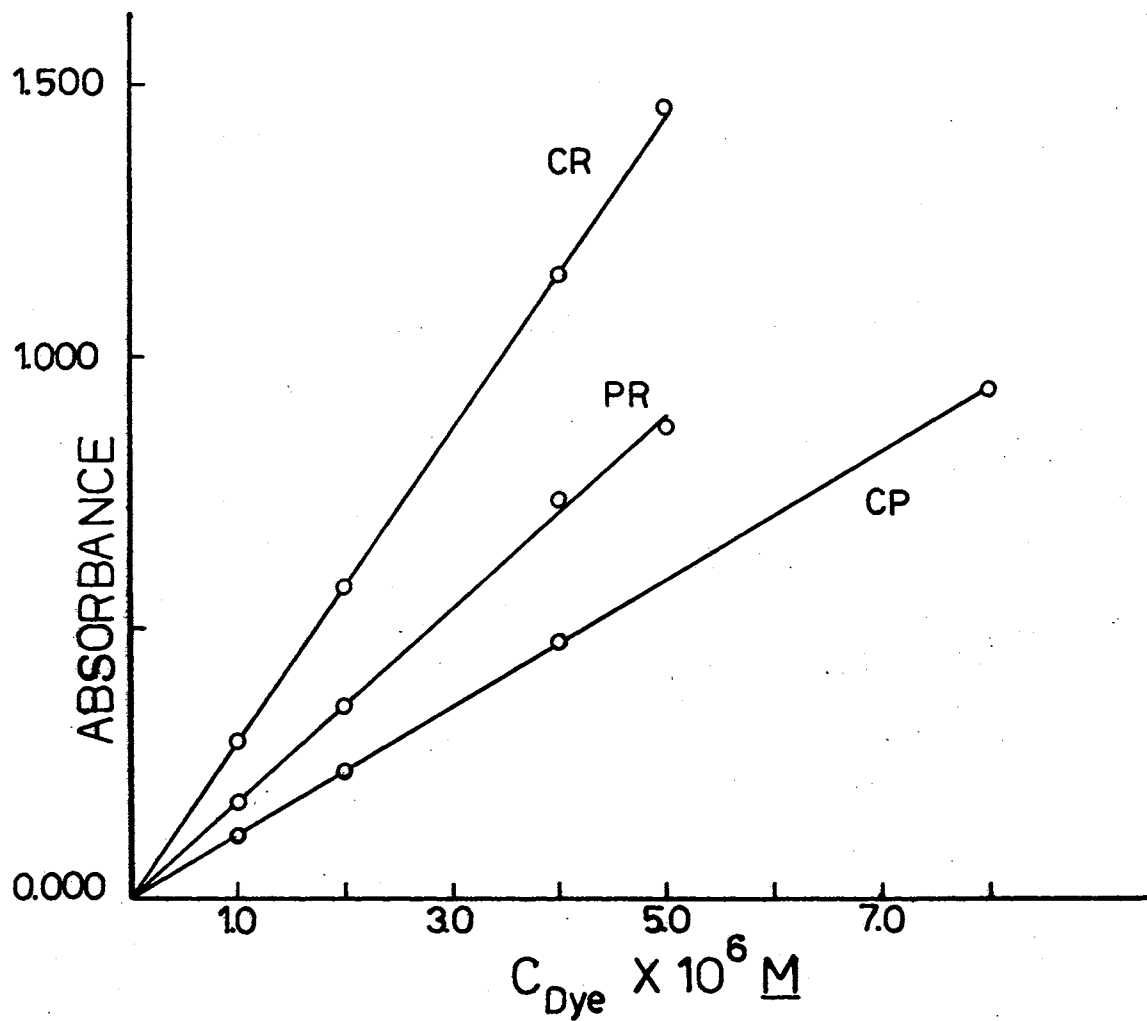1.0 x $10^{-5}\underline{M}$ Dyes, pH 9.20, 1.0 cm cells

Figure 7. Typical Beer's Law Plots for Cresol Red, Phenol Red, and Cresol Purple
pH 9.20, 572 nm, 5.0 cm cells

Equilibrium determinations were effected by measuring the absorbances of each mixture at the different analytical wavelengths. These values and the corresponding molar absorptivities were used in conjunction with sets of proportional equations which were solved simultaneously to compute the concentrations values being sought. Experimental results are listed in Tables III, IV, V, and VI.

Kinetic Determination of A Basic Dye Mixture

The reaction scheme proposed for the oxidation of sulfonephthalein dyes (Equations 4.4 and 4.5) is also proposed for the oxidation of the singly charged cationic form of basic triphenylmethane dyes in acidic soltuions, pH 3.0 to 6.0. However, $H_4IO_6^-$ rather than $H_3IO_6^{2-}$ is the predominate periodate species over this pH range (12). In basic solutions there seems to be only a small difference between the rates of the uncatalyzed and catalyzed oxidation of dyes of this type. For example, the pseudo-first-order rate constants for the uncatalyzed and catalyzed reaction of malachite green at pH 9.2 (borate buffer) are 0.0156 min^{-1} and 0.0182 min^{-1} respectively. These values were determined using 1.0 x 10^{-6} $\underline{M}$ Mn(II), 3.5 x 10^{-6} $\underline{M}$ dye, and 1.0 x 10^{-3} $\underline{M}$ periodate.

Some kinetic applications of the oxidation of malachite green by the manganese-periodate oxidant have been described in references (16, 47, 48, 49, and 28). Examination of the reaction curves for pure malachite green and pure brilliant green (Figure 8) suggested that the kinetic method of proportional equations could be readily applied to the determination of mixtures of these dyes. Reaction of a mixture, however, revealed that when combined malachite green and brilliant green were not oxidized according to the constant fractional life
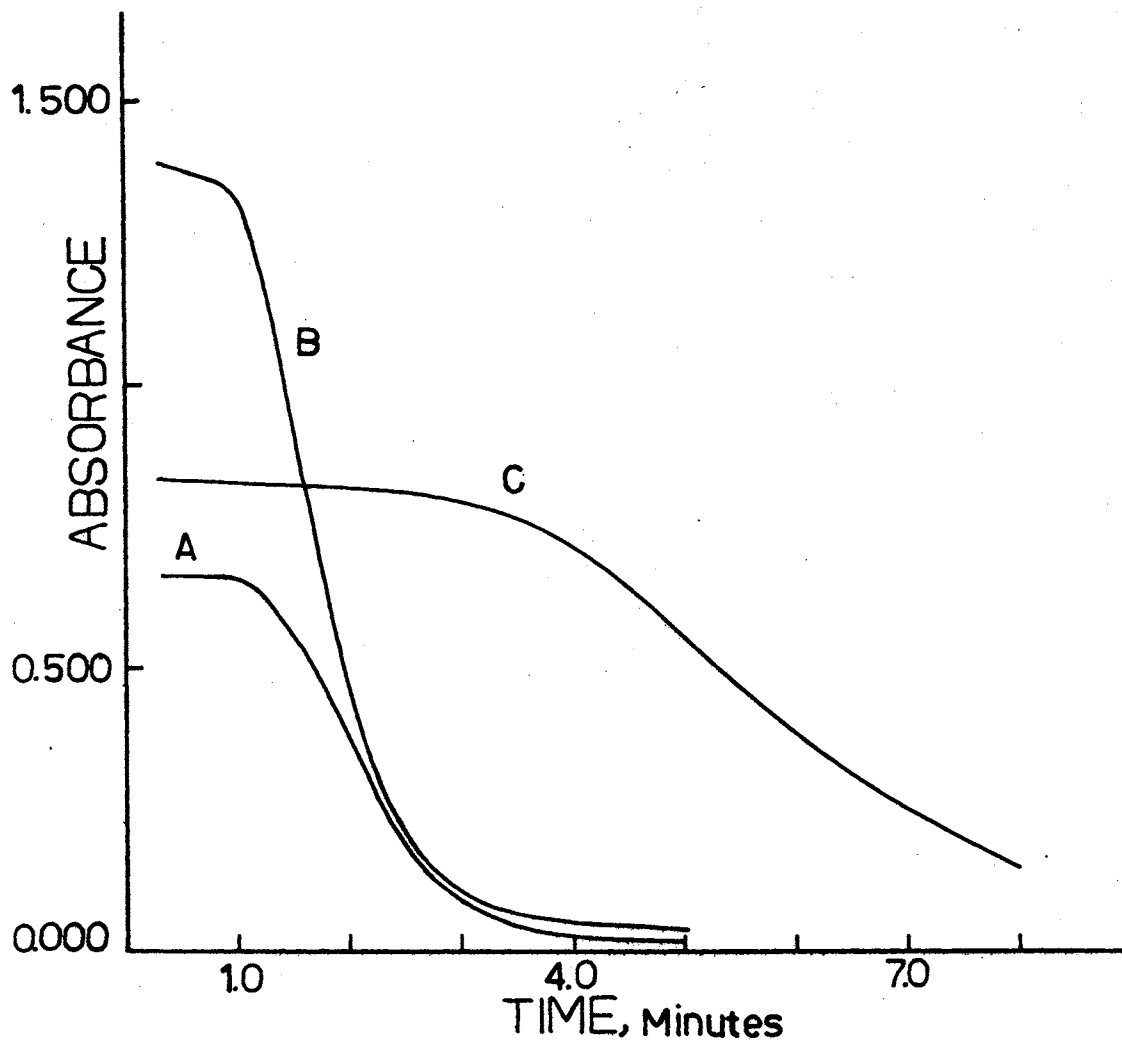
Figure 8. Absorbance Versus Time Curves for Brilliant Green and
Malachite Green in Acetate-Phosphate Buffer

A: 1.0 x 10^{-5} M MG, B: 1.0 x 10^{-5} M BG,
C: 1.0 x 10^{-5} M MG - 1.0 x 10^{-5} M BG

5.0 x 10^{-6} M Mn(II), 0.1% NaIO$_4$, pH 3.50, 620 nm
1.0 cm cells

principle. The two dyes did not react independently when mixed. The reaction of the faster reacting dye, malachite green, appeared to accelerate the reaction of brilliant green to the extent that the mixture reacted as if it were a unique species. Since the method of proportional equations is not applicable under circumstances of this kind, a series of experiments were performed in an effort to arrive at a set of conditions suitable for analysis. These studies are described below. Figure 9 shows the aqueous absorption spectra of malachite green and brilliant green. The structure of the dyes are illustrated in Appendix B.

Effect of Mn(II) Ion Concentration

At pH 3.5, runs were made using Mn(II) ion concentrations of 1.0 x 10^{-5} $\underline{M}$ and 5.0 x 10^{-6} $\underline{M}$. At the lower manganese ion concentration less differentiation occurred in the reaction rates of the two dyes, however, the rate of the mixture more closely approached that which would result if the two dyes were reacting independently.

Effect of pH

Using a Mn(II) ion concentration of 5.0 x 10^{-6} $\underline{M}$, reactions were run at pH 3.0, 3.5, and 4.5. No particular advantage was realized at either pH 3.0 or 3.5. A pronounced decrease in rate differentiation occurred at pH 4.5. Therefore, studies were not made in solutions which were more basic. Since both dyes, malachite green and brilliant green, exist primarily as the yellow, double charged, cation when the hydrogen ion concentration of their solution is greater than 10^{-3} $\underline{M}$ (3, 17), the use of solutions more acidic than pH 3.0 was not feasible.
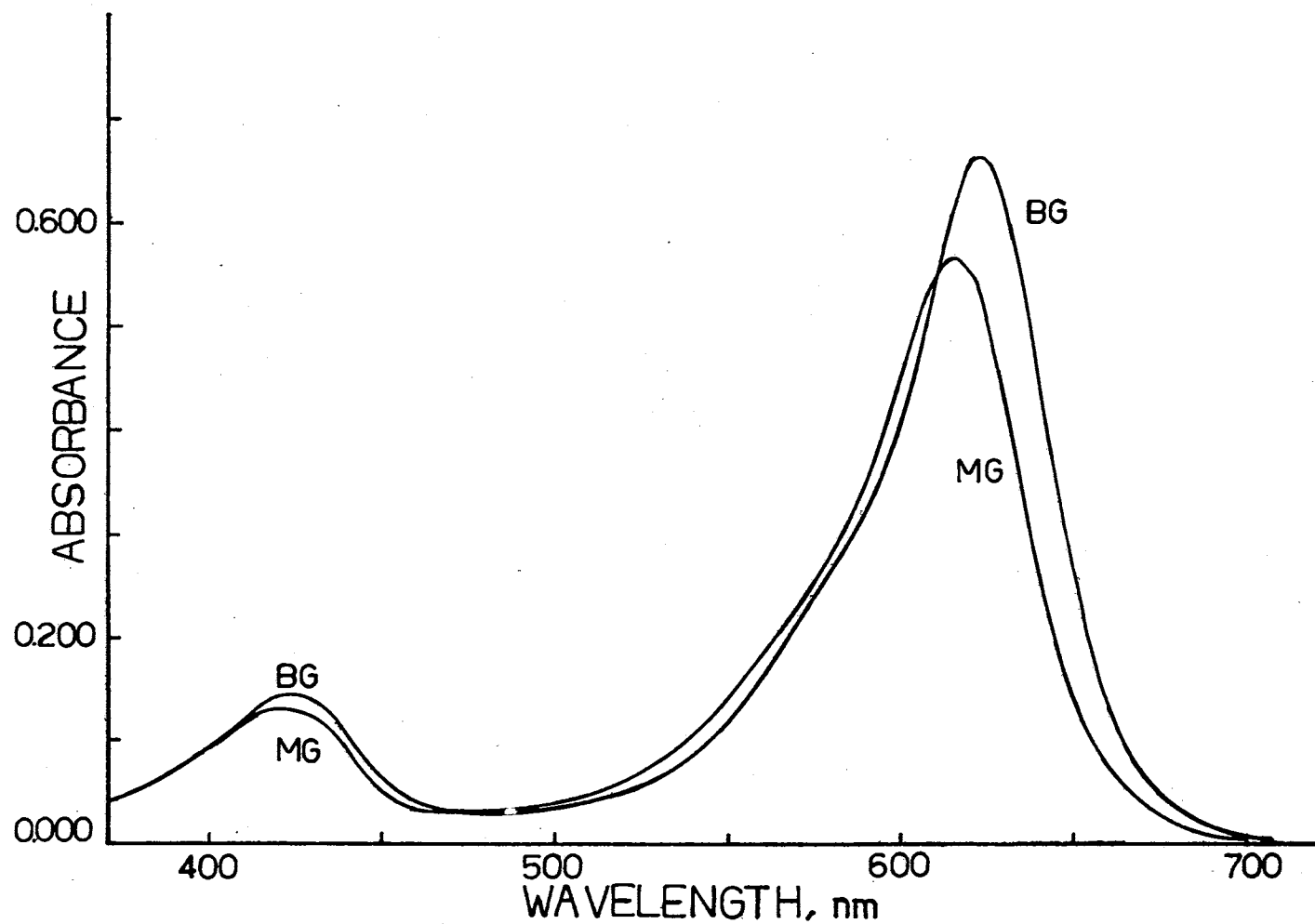
Figure 9.   Aqueous Spectra of Brilliant Green and Malachite Green

2.0 x 10^{-6} $\underline{M}$ Dyes, pH 4.10 (Acetate Buffer), 5.0 cm cells

Effect of Buffer Composition

In addition to the acetate-phosphate, reactions were carried out in three other buffers; citric acid-phosphate, pH 4.0; HCl-biphthalate, pH 4.0; and acetate, pH 4.1, ionic strength 0.01. The citrate-phosphate buffer completely inhibited the oxidation of the dyes, while rate differentiation for the pure dyes was greatly increased by the other buffers. Synergistic effects, however, prevented analysis of the dye mixtures. (See Figures 10 and 11).

The dyes were reacted at pH 3.5 using the acetate-phosphate buffer at one-half ionic strength. Rate differentiation was less than that observed in the "full-strength" buffer.

Effect of Solvent Composition

Spectra of the two dyes were run in 30% solutions of each of the following solvents: acetone, dimethylsulfoxide, dioxane, and dimethylformamide. Except for increases in peak heights, the spectra of the dyes were virtually unchanged by the mixed solvents. The molar absorptivity of brilliant green was increased from 40% to 50%, the largest increased occurring in the acetone mixture.

Oxidation of the two dyes and their mixture in 30% acetone gave results that were very similar to those obtained in 100% aqueous medium. The acetate buffer, pH 4.1, was used in these studies.

Other Effects

At pH 3.5, "runs" were made in which the order of combining reactants was altered. Instead of combining (dye plus Mn(II) ion) and (periodate ion plus buffer) the Mn(II) ion, periodate ion, and buffer
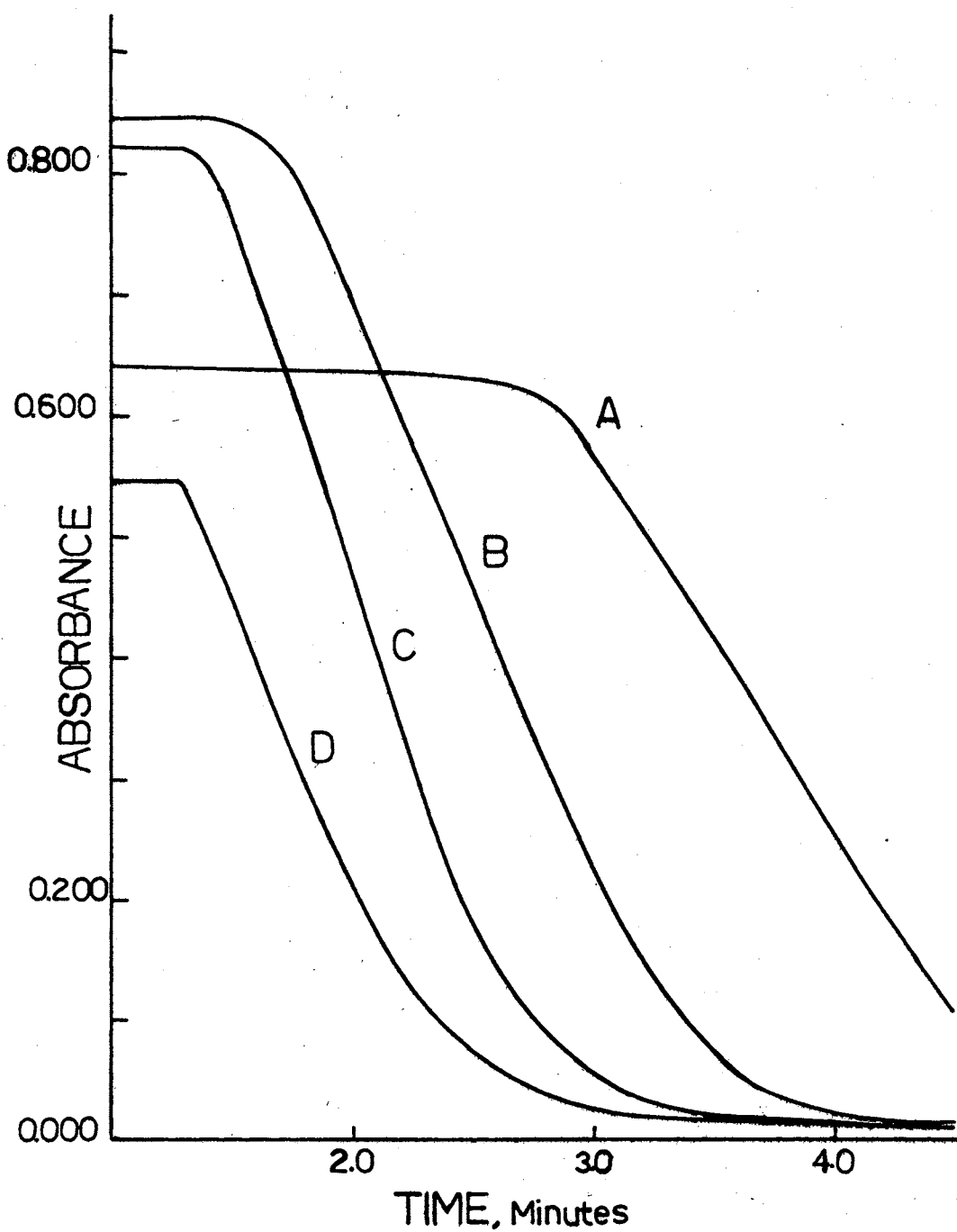
Figure 10. Absorbance Versus Time Curves for Brilliant Green and
Malachite Green in Acetate Buffer

A: 2.0×10^{-6} M BG, B: 2.0×10^{-6} M BG - 8.0×10^{-7} M MG,
C: 8.0×10^{-7} M BG - 2.0×10^{-6} M MG, D: 2.0×10^{-6} M MG

5.0×10^{-6} M Mn(II), 0.1% $NaIO_4$, pH 4.10, 620 nm, 5.0 cm cells
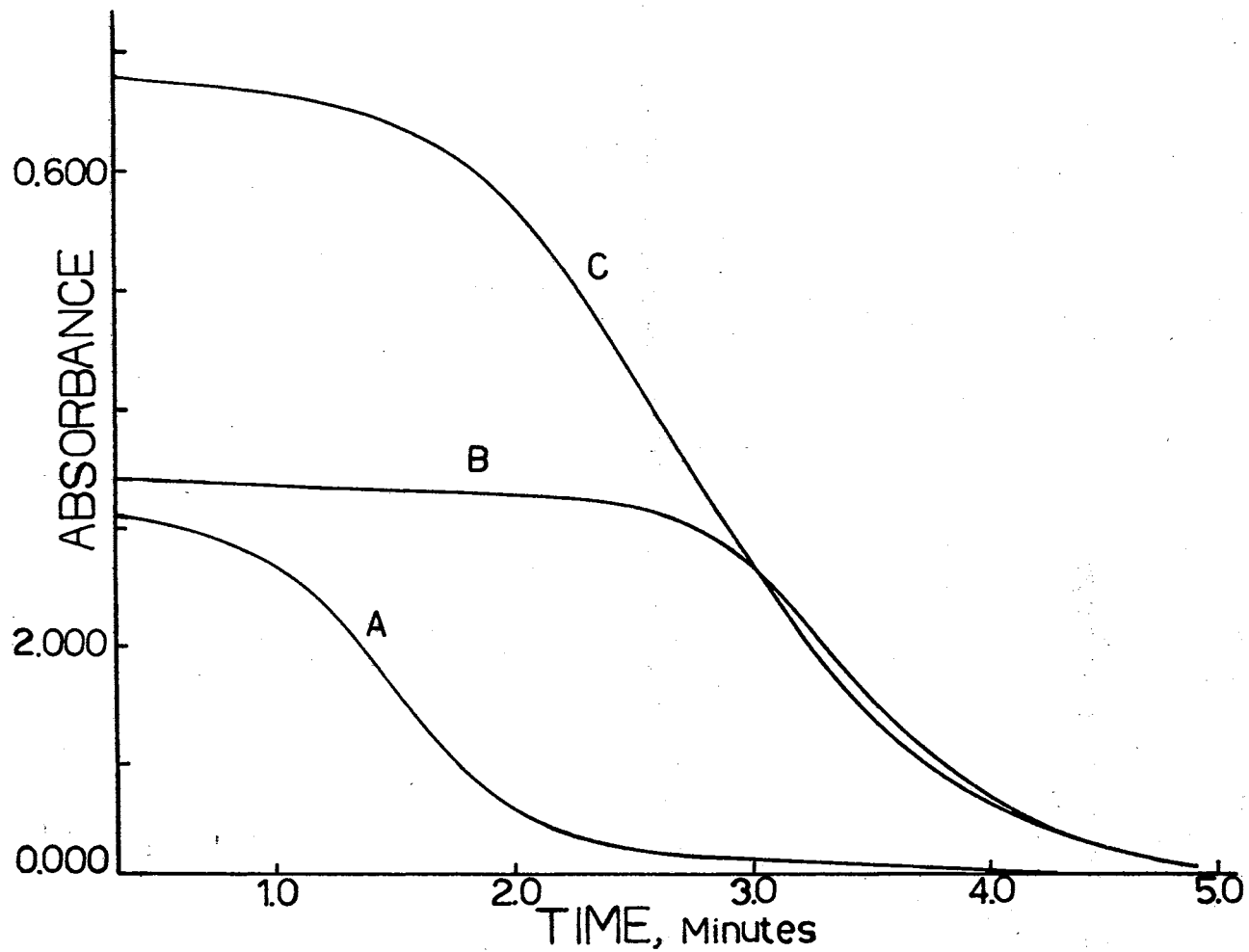
Figure 11. Absorbance Versus Time Curves for Brilliant Green and Malachite Green in Phthalate Buffer

A: 1.0×10^{-5} $\underline{M}$ MG, B: 1.0×10^{-5} $\underline{M}$ BG, C: 1.0×10^{-5} $\underline{M}$ MG $- 1.0 \times 10^{-5}$ $\underline{M}$ BG

1.0×10^{-5} $\underline{M}$ Mn(II), 0.1% $NaIO_4$, pH 4.00, 620 nm

were combined and then reacted with the dye. The latter procedure resulted in rate curves having shorter induction periods but otherwise not significantly different from those obtained previously. The shorter induction periods possibly resulted from the fact that a larger ratio of Mn(III) to Mn(II) was present in the system when the dyes were brought into reaction with the oxidant.

Determinations of ethylenediamine-N,N,N',N',-tetraacetic acid (EDTA) based on its inhibitory effect on the Mn(II)-catalyzed oxidation of malachite green have been described (47, 48). In each of these works, however, it was observed that under certain conditions the presence of EDTA produced a rate accelerating effect rather than inhibition. Included as part of the study reported herein was an attempt to use this catalytic effect as a means to resolve mixtures of malachite green and brilliant green. Two series of experiments were conducted at pH 3.5. One in which the ratio of EDTA to Mn(II) was varied at the 10^{-6} $\underline{M}$ level. In the other, various methods of combining the reactants was explored. While each series of experiments yielded different rate curves, none proved to be analytically useful.

Malachite green perchlorate was used for nearly all studies described above. A few "runs" were made with malachite green hydrochloride and malachite green oxalate. Except for shorter induction periods when the oxalate was used these forms of malachite green behaved in the same manner as the perchlorate.

Treatment of Errors

The values for all constants, kinetic proportionality constants or molar absorptivities, used for the analysis of mixtures, were determined

by plotting an experimentally measured parameter versus the concentration of pure dye. The slopes of these plots, m, were determined by linear least squares fits from the relation

$$m = \frac{N\Sigma(X_i Y_i) - \Sigma X_i \Sigma Y_i}{N\Sigma X_i^2 - (\Sigma X_i)^2} \tag{4.16}$$

and taken to be the "best" values for the constants. In this eqation, N is the total number of measurements. Coordinates of the individual measurements are represented by X_i and Y_i. The standard deviations of the slopes, s_m, were calculated from the equation (2)

$$s_m = s_y \left(\frac{N}{N\Sigma X_i^2 - (\Sigma X_i)^2}\right)^{\frac{1}{2}} \tag{4.17}$$

where

$$s_y = \left(\frac{\Sigma(\delta Y_i)^2}{N-2}\right)^{\frac{1}{2}}. \tag{4.18}$$

The value of δY_i is given by

$$\delta Y_i = Y_i - (b + mX_i) \tag{4.19}$$

where b is the intercept of the line of best fit. Graphically, δY_i is the vertical distance from the point $(Y_i X_i)$ to the straight line of best fit.

If P is a measured parameter and its value depends on several independent variables, x, y, x, then $P = f(x,y,z)$. The general equation for the propagation of the error in P is

$$s_P^2 = \left(\frac{\partial P}{\partial X}\right)^2 s_X^2 + \left(\frac{\partial P}{\partial Y}\right)^2 s_Y^2 + \left(\frac{\partial P}{\partial Z}\right)^2 s_Z^2 \tag{4.20}$$

The quantity s^2 is termed the variance.

Selective Kinetic Determination of Cresol Red

From Equation (4.15) it can be said that $C_{CR} = f(K_{CR}, \Delta A)$, where C_{CR}

is the initial concentration of cresol red. Applying Equation (4.20), and using CR to represent C_{CR}, the variance of the cresol red concentration is

$$s^2_{CR} = (\frac{\partial CR}{\partial K_{CR}})^2 \; s^2_{K_{CR}} + (\frac{\partial CR}{\partial \Delta A})^2 \; s^2_{\Delta A} \qquad (4.21)$$

Taking the partial derivatives gives

$$s^2_{CR} = (\frac{-\Delta A}{K^2_{CR}})^2 \; s^2_{K_{CR}} + (\frac{1}{K_{CR}})^2 \; s^2_{\Delta A} \qquad (4.22)$$

To evaluate s^2_{CR}, the value of K_{CR} was calculated by Equation (4.16), the value of $s_{K_{CR}}$ from Equation (4.17), the value $s_{\Delta A}$ was computed from replicate measurements, and ΔA was taken as the mean of the replicates. For all error propagation studies described herein, this procedure was used to evaluate all constants, the standard deviation of constants, the measured parameters (A or ΔA), and the standard deviation of these parameters. Values for s_{CR}, the standard deviation of the cresol red concentration, are reported in Table II.

Kinetic Determination of Cresol Red and Phenol Red

The variance of the cresol red concentration was determined in the exact manner as described in the previous section. Since both dyes are determined independently the variance of phenol red, s^2_{PR}, is computed from an equation analogous to Equation (4.22). Values for the standard deviations, s_{CR} and s_{PR}, are listed in Table IV.

Kinetic and Equilibrium Determinations of Cresol Purple and Phenol Red--Equilibrium Determination of Cresol Red and Phenol Red

Equations (4.10) and (4.11) are similar to those generally used for multicomponent analysis by the method of proportional equations. In

the general case, constants in the equations may be either kinetic constants or molar absorptivities depending on the approach used for analysis. Using P and P' instead of ΔA_{XY} and $\Delta A_{XY}'$, to represent the measured parameter, solutions to the general equations are

$$[X]_o = \frac{PK_Y' - P'K_Y}{K_X K_Y' - K_X' K_Y} \qquad (4.23)$$

and

$$[Y]_o = \frac{P'K_X - PK_X'}{K_X K_Y' - K_X' K_Y} \qquad (4.24)$$

From these equations it can be said that $[X]_o$ and $[Y]_o = f(K_X, K_X', K_Y, K_Y', P, P')$. Values for $s^2_{[X]_o}$ and $s^2_{[Y]_o}$ can be calculated by use of equations which are analogous to Equation (4.20), but have six terms each. As an example, using X to represent $[X]_o$, the variance of $[X]_o$ is evaluated by

$$s^2_X = \left(\frac{\partial X}{\partial K_X}\right)^2 s^2_{K_X} + \left(\frac{\partial X}{\partial K_X'}\right)^2 s^2_{K_X'} + \left(\frac{\partial X}{\partial K_Y}\right)^2 s^2_{K_Y}$$
$$+ \left(\frac{\partial X}{\partial K_Y'}\right)^2 s^2_{K_Y'} + \left(\frac{\partial X}{\partial P}\right)^2 s^2_P + \left(\frac{\partial X}{\partial P'}\right)^2 s^2_{P'}, \qquad (4.25)$$

Results from calculations of this type are included in Tables IV and V. General solutions for the partial derivatives of the various terms in the two error propagation equations are given in Appendix C.

In order to determine which variables contributed most to the errors in $[X]_o$ and $[Y]_o$, values for the six terms of the error propagation equations were compared. In general, it was found that the values for most of the terms in an equation differed by less than two orders of magnitude. As could be expected, the variance contributions depended on factors such as the relative sizes of the constants and the relative standard deviations of the parameters, P and P'.

Conclusions

The studies described in this thesis demonstrate that a kinetic
method of analysis can be successfully employed for the "in situ"
multicompenent determination of dye mixtures whose components have very
similar absorption spectra and structures which differ only by the
position of a functional group or the type substituents present. The
accuracy and precision of the kinetic results compare well with those
obtained using a comparable equilibrium method. In general, the experi-
mental results obtained from this research agree with those which can be
expected from calculations based on error propagation.

In order to determine the minimum accuracy and precision of the
binary analyses described in this thesis, eight replicate determinations
were made for several mixtures. The mixtures selected for this treatment
were ones which were most difficult to determine by the methods employed.
It was found that for kinetic determinations of mixtures of cresol red
and phenol red the accuracy of the mean ranged from about (0 to 5%) with
a relative precision of (4 to 8%). The accuracy and precision for
equilibrium determinations of these mixtures were about (0 to 14%) and
(0 to 4%) respectively. For mixtures of cresol purple and phenol red,
an accuracy of (0 to 5%) was obtained using the kinetic procedure. The
precision was about (2 to 5%). For the equilibrium determinations an
accuracy of (0 to 3%) and a precision of about 1% were obtained.

Results reported in this thesis show that a kinetic approach to
analysis can offer some definite advantages over a more conventional
equilibrium approach. For example, the determination of cresol red in
mixtures (Table I) by the equilibrium MPE would require prior knowledge
of the identity of each dye in the mixture. In case of the third mix-

ture in the same Table, not only must the dyes be identified, but the concentrations of bromocresol purple and bromocresol green have to be known. The kinetic method, however, does not require these prior determinations.

Another advantage presented by the kinetic method and shown in Tables III, IV, V, and VI is that it can be readily applied in cases where background absorbance is caused by unknown unreactive impurities other than dyes. This advantage stems from the fact that the kinetic method is based on the measurement of relative changes in absorbances rather than absolute absorbance measurements as in the equilibrium absorptiometric MPE.

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STRUCTURES OF SOME SULFONEPHTHALEIN DYES
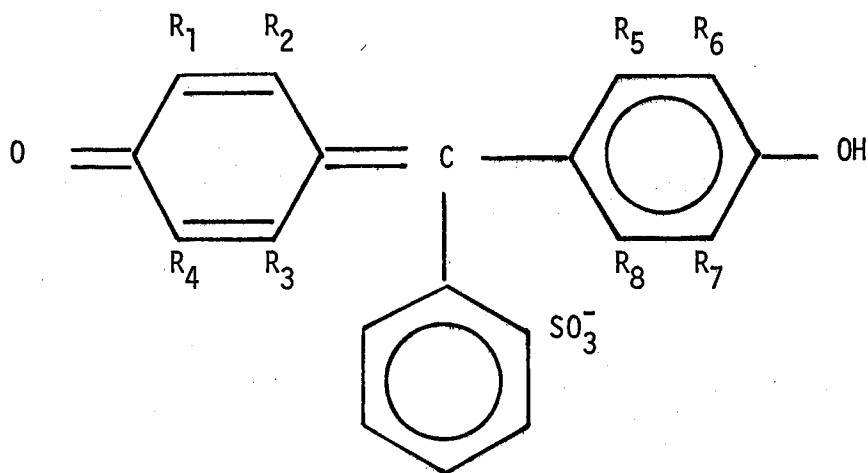
All R's: -H, otherwise specified.

R_2, R_8: -CH_3, R_1, R_4, R_6, R_7: -Br; BROMOCRESOL GREEN

R_1, R_7: -CH_3, R_4, R_6: -Br; BROMOCRESOL PURPLE

R_1, R_4, R_6, R_7: -Br; BROMOPHENOL BLUE

R_4, R_6: -CH-$(CH_3)_2$, R_1, R_7: -Br, R_2, R_8: -CH_3; BROMOTHYMOL BLUE

R_2, R_4, R_6, R_8: -CH_3, R_1, R_7: -Br; BROMOXYLENOL BLUE

R_1, R_7: -Cl; CHLOROPHENOL RED

R_3, R_8: -CH_3; CRESOL PURPLE

R_1, R_7: -CH_3; CRESOL RED

R_4, R_6: -CH-$(CH_3)_2$, R_2, R_8: -CH_3; THYMOL BLUE

R_2, R_4, R_6, R_8: -CH_3; XYLENOL BLUE

APPENDIX B

STRUCTURES OF BRILLIANT GREEN AND MALACHITE GREEN

$$\left[(R)_2 \overset{\oplus}{N} = \left\langle \text{ring} \right\rangle = C - \left\langle \text{ring} \right\rangle - N(R)_2 \right] A^-$$

Brilliant Green

    $R = -C_2H_5$; $A = HSO_4^-$.

Malachite Green

    $R = -CH_3$; $A = Cl^-$, ClO_4^-, or $C_2O_4^{2-}$.
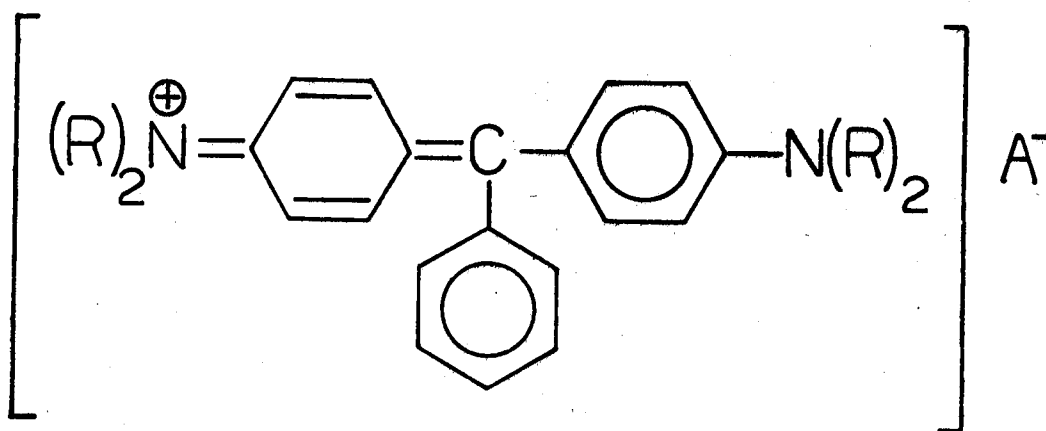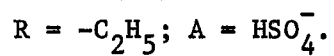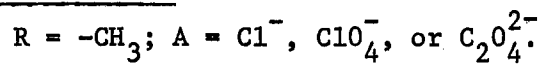
APPENDIX C

SOLUTIONS TO PARTIAL DERIVATIVES USED IN ERROR

PROPAGATION EQUATIONS FOR THE METHOD OF

PROPORTIONAL EQUATIONS

For simplification, let $X = [X]_o$, $Y = [Y]_o$, and $D = (K_X K_Y' - K_Y K_X')$.

$$\left(\frac{\partial X}{\partial K_X}\right) = -\frac{K_Y'(K_Y'P - K_Y P')}{D^2} \tag{A.1}$$

$$\left(\frac{\partial X}{\partial K_X'}\right) = +\frac{K_Y(K_Y'P - K_Y P')}{D^2} \tag{A.2}$$

$$\left(\frac{\partial X}{\partial K_Y}\right) = -\frac{K_Y'(K_Y P' - K_X'P)}{D^2} \tag{A.3}$$

$$\left(\frac{\partial X}{\partial K_Y'}\right) = -\frac{K_Y(K_X'P - K_X P')}{D^2} \tag{A.4}$$

$$\left(\frac{\partial X}{\partial P}\right) = \frac{K_Y'}{D} \tag{A.5}$$

$$\left(\frac{\partial X}{\partial P'}\right) = -\frac{K_Y}{D} \tag{A.6}$$

$$\left(\frac{\partial Y}{\partial K_X}\right) = \frac{K_X'(K_Y P' X - K_Y'P)}{D^2} \tag{A.7}$$

$$\left(\frac{\partial Y}{\partial K_X'}\right) = \frac{K_X(K_Y'P - K_Y P')}{D^2} \tag{A.8}$$

$$\left(\frac{\partial Y}{\partial K_Y}\right) = \frac{K_X'(K_X'P - K_XP')}{D^2} \qquad (A.9)$$

$$\left(\frac{\partial Y}{\partial K_Y'}\right) = -\frac{K_X(K_X'P - K_XP')}{D^2} \qquad (A.10)$$

$$\left(\frac{\partial Y}{\partial P}\right) = \frac{K_X'}{D} \qquad (A.11)$$

$$\left(\frac{\partial Y}{\partial P'}\right) = -\frac{K_X}{D} \qquad (A.12)$$

VITA

Gerald Lloyd Ellis

Candidate for the Degree of

Doctor of Philosophy

Thesis: KINETIC AND EQUILIBRIUM SIMULTANEOUS ANALYSES OF SOME SUL-
FONEPHTHALEIN DYE MIXTURES BY THE METHOD OF PROPORTIONAL
EQUATIONS

Major Field: Chemistry

Biographical:

Personal Data: Born in Laurel, Mississippi, December 26, 1935, the
son of Leander T. and Regina J. Ellis; married to Martha
Levada Simmons on June 4, 1966.

Education: Graduated from Oak Park High School, Laurel, Mississippi
in June 1954; received Bachelor of Science degree from
Tennessee State University, Nashville, Tennessee, June 1958,
with a major in Chemistry; received Master of Science degree
from Pennsylvania State University, University Park,
Pennsylvania, December 1961, with a major in Chemistry; com-
pleted requirements for Doctor of Philosophy degree, Oklahoma
State University in May, 1973.

Professional Experiences: Assistant Professor of Chemistry,
Mississippi Valley State College, Itta Bena, Mississippi,
January, 1962, to May, 1965; Assistant Professor of Chemistry,
Grambling College, Grambling, Louisiana, June, 1965, to August,
1968, and September 1971 to present.

Membership in Professional Societies: Member of Phi Lambda Upsilon,
Honorary Chemical Society, Member of American Chemical Society.