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AN INDIRECT SPECTROPHOTOMETRIC METHOD FOR EXPANSION OF THE OPTIMUM CONCENTRATION RANGE

by

Henry D. Mitchell

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Western Michigan University Kalamazoo, Michigan December 1967
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THE PROBLEM AND ITS BACKGROUND

With the development of spectrophotometry, instrumental and experimental parameters have been studied in great detail in an effort to determine the limits of accuracy and precision, and the specific sources of error due to instrumental design and experimental technique. This investigation was restricted to only those considerations of experimental technique which are related to the precision and accuracy of spectrophotometric measurements.

Terms and Definitions

Two systems of nomenclature have been used. The older system (1) is slowly being replaced by a more modern system which takes into account the technological advances in cell and instrument design. The new terminology and definitions (2) are given in Table 1.
Table 1. Nomenclature in spectrophotometry.

Transmittance, \( T = \frac{P}{P_0} \)
Absorbance, \( A = - \log T = \log \frac{1}{T} \)
Absorptivity, \( a = \frac{A}{bc} \)
Absorptance, \( 1 - T \)
Transmittancy, \( T_s = \frac{T_{soln}}{T_{solv}} \)
Absorbancy, \( A_s = - \log T_s = \log \frac{1}{T_s} \)

Figure 1 illustrates the terms given in Table 1.
The definitions for transmittancy and absorbancy apply
for rectilinear transmission of homogeneous radiant
energy through a sample diluted with a solvent.

Sources of Error in Photometric Measurements

Design characteristics

The precision of photometric measurements as it is
related to the design characteristics of several
commercial spectrophotometers has been discussed by
Gridgeman (3) and Hiskey (4). Many of these limitations
are attributable to the instruments themselves and are
not necessarily a limitation of spectrophotometric
methods in general.

Concentration effects

Ayres (5) and Ringbom (6) have studied the effects
of concentration on the precision and accuracy of analyses. These effects result from the fact that concentration is a logarithmic function of transmittance, the quantity which is determined directly by most spectrophotometers. Consequently a given uncertainty in the transmittance measurement gives rise to varying concentration errors depending upon the actual transmittance value being measured. This may be seen in Figure 2. Ringbom has shown mathematically that the optimum transmittance occurs at 36.8 %T. Stray radiation becomes a problem at high concentration, while multiple reflection path errors, $P_{mr}$ in Figure 1, become a problem at low concentration. The former results in a negative deviation from Beer's Law, while the latter produces a positive deviation.

**Temperature and refractive index effects**

A study of the deviations from the Beer-Lambert-Bouguer relationship with particular emphasis on the effects of temperature and refractive index has been made (7). Variation in volume with temperature obviously will have an effect on concentration. The refractive index differences between air, the cell material, and the solution may cause divergence of the light beam, resulting in a decrease in the radiant energy reaching the detector.
Figure 2. Concentration effects on the precision of spectrophotometric measurements.
Stray radiant energy and slit width effects

A great majority of commercial spectrophotometers have equal entrance and exit slits. A discussion of slit width effects for this case and the case with unequal slits has been given by Mellon (8). Finite slit widths may often pass a wider wavelength band than is desired. It must be remembered that monochromaticity is assumed in the derivation of Beer's Law. A slit which allows the transmission of wavelengths other than the desired monochromatic radiation will cause deviation from Beer's Law. The effects of finite slit widths upon a measurement may be seen in Figure 3. Transmittance errors can occur in measurement at an absorption maximum, especially at high absorbance when wide slits are required. Negative deviations from Beer's Law result.

Figure 3. Finite slit width effects on the measurement of transmittance.

These errors are smaller for solutions of lower absorbance since smaller slit widths may be used. The
slit width actually used will depend on the desired signal-to-noise ratio, sensitivity, and resolution. Studies confirming these slit width effects have been reported (9, 10).

Miscellaneous errors

Hamilton (11) has discussed errors in the setting and reading of the zero and 100 percent points on the galvanometer for both high and low absorbance systems. Errors arising from differences of opacity between the sample and reference solutions have also been reported (12).

Techniques to Minimize Errors

Differential methods

Differential spectrophotometry has been developed as one method to help minimize some of the previously discussed errors common to conventional spectrophotometric methods. Bastian and coworkers (13) have compared the differential method of analysis to spectrophotometry. A study of the effects of finite slit width and stray radiation in differential spectrophotometry has been reported by Lothian (14).

Reilley and Crawford (9) have reported three differential methods which utilize the technique of scale
expansion to minimize errors. Of the three methods, one
is applicable to solutions of low absorbance, while
another gives good precision for solutions of high absorb-
ance. The third, the "ultimate" precision method, gives
relatively good precision over most of the absorbance
scale.

**Indirect methods**

Indirect spectrophotometry is another technique
which has been used to minimize many of the previously
discussed errors. With this technique the unknown, \(X\),
is allowed to react with an excess of a chromophoric
species, \(S\). The excess of the chromophoric species
remaining, after reaction, is then determined. Provided
that the stoichiometry of the reaction between the un-
known and chromophoric species is known, the amount of
unknown may then be determined. The reaction may be
represented in general terms as follows:

\[
X + (nS + S) = Y + S
\]  

The errors inherent in the chromophoric system of
the unknown may be eliminated and replaced by those of
the more desirable chromophoric system, \(S\).

Lothe (15) has reported the findings of a study on
precision in indirect spectrophotometry as it is related
to relative errors as a function of transmittance and
absorbance values. Reilley and Hildebrand (16) have
devised four modifications of the indirect method. Their
modifications involve different ways of setting the zero
to one hundred percent transmittance scale with various
combinations of reference and unknown solutions.

Advantages of the Indirect Differential Method

Optimum concentration

Considering the numerous sources of errors previously
discussed, one might wish to experimentally determine the
optimum concentration. The inflection point of a Ringbom
plot (6) prepared from experimental data should correspond
to the optimum concentration value. Methods have been
reported (7) for calculating the relative error in ordinary
colorimetric work, for the case where the light
transmittance characteristics of the solvent and unknown
solutions are compared.

Precision methods

Precision methods can be applied to indirect differ-
ential analysis just as to ordinary differential analysis
(17, 9). Consequently, the zero and one hundred percent
transmittance points may be chosen with standards to
yield a scale expansion in the vicinity of the unknown
absorbance.
Contaminants in reagents and solutions

The indirect differential method has an advantage over ordinary spectrophotometric analysis in that extremely pure reagents are not always required. Even when the reagents or solutions contain small amounts of the substance being determined, an accurate analysis can be made. This is possible because the reference and sample solutions are made from the same reagents. It is only the effect of the unknown substance added to the sample solution which is measured. Howell and Boltz (18) have demonstrated this with a procedure for the determination of ammonia. It was shown that the use of ammonia-free distilled water and reagents was unnecessary.

Unstable chromophores

The above workers (18) also were able to show with their procedure for the determination of ammonia that the indirect differential method minimizes errors due to instability of the chromophore. In this system both the reference and sample contain the relatively unstable chromophore, hypobromite ion. The differential absorbance, \( \Delta A \), due to the reaction of some of the absorbing species in the sample solution with the unknown, remains essentially constant as the absorbing species undergoes decomposition in both the reference and sample solutions at nearly equal rates.
Molar amplification

Howell (19) has shown that a molar amplification may be achieved by judicious choice of the chromogenic reagent. Two desirable features of the chromogenic reagent to be sought are a high molar absorptivity, and a stoichiometry such that more than one mole of chromogenic reagent per mole of analyte is consumed in the reaction. The reaction studied by Howell was that of chlorine dioxide with excess ferrous ion and subsequent development of the tris-1, 10-phenanthroline-iron (II) complex. The ferrous complex has a molar absorptivity of 11,100 and consequently gives an effective molar absorptivity of 55,500 for chlorine dioxide.

Specificity

Specificity is also a desirable characteristic which can often be incorporated into indirect methods. The unpublished results of Koning (20) reveal the development of a method for the analysis for carbon monoxide. A sample of air containing carbon monoxide is passed over heated nickel. The resulting nickel tetracarbonyl gas is trapped and measured spectrophotometrically. Other common constituents of air samples were not found to interfere.
Extension of the optimum concentration range

From results of the present work it is postulated that the optimum concentration range may be extended by use of an indirect differential technique.

Referring to Figure 4 an equation may be derived for extending the optimum concentration range as follows:

In principle it is desired to determine

\[-\log \frac{P}{P_0} = A\]  \[2\]

however, what actually is being measured is

\[-\log \frac{P}{P'}\]  \[3\]

It can be seen that

\[-\log \frac{P}{P'} = -\log \frac{P_0}{P_0'}\frac{P_0'}{P_0} = \left[ -\log \frac{P}{P_0} \right] - \left[ -\log \frac{P'}{P_0} \right]\]  \[4\]

Instrumental conditions can be adjusted such that

\[P_0' = P_0\]  \[5\]

Substituting equation \[5\] into the second term of equation \[4\] we obtain

\[-\log \frac{P}{P'} = \left[ -\log \frac{P}{P_0} \right] - \left[ -\log \frac{P'}{P_0} \right]\]  \[6\]

By definition of absorbance we see that

\[-\log \frac{P}{P_0} = A\]  \[7\]

and

\[-\log \frac{P'}{P_0} = A'\]  \[8\]

where \(A\) and \(A'\) are the absorbances of the solutions in the sample and reference beams respectively.

Substituting equations \[7\] and \[8\] into equation \[6\]
leads to

\[- \log \frac{P}{P'} = A - A' = \Delta A \quad [9]\]

Therefore the signal which is actually measured, \(\Delta A\), is the difference of the absorbances of the solutions in the sample and reference beams.

The Beer-Lambert-Bouguer relationships for this case are:

\[A = abc \quad [10]\]

and

\[A' = a'b'c' \quad [11]\]

where \(a\) and \(a'\) are the absorptivities, \(b\) and \(b'\) are the path lengths in centimeters, and \(c\) and \(c'\) are the concentrations of the absorbing species. The primes are used to denote the system in the reference beam, while the unscripted symbols refer to the system in the sample beam.

Certain restrictions are generally imposed on the simultaneous use of equations \([10]\) and \([11]\). These are that \(c\) and \(c'\) refer to concentrations of the same absorbing species, and also that

\[c \geq c' \quad [12]\]

Since \(c\) and \(c'\) refer to concentrations of the same absorbing species, then

\[a' = a \quad [13]\]

Also, the absorption cells can readily be selected such
that
\[ b' = b \] \[14]\nSubstituting equations \[10\], \[11\], \[13\], and \[14\] into equation \[9\] we obtain
\[ A = ab(c - c') \] \[15\]
Consider the general reaction
\[ X + rY_{(xs)} = Z + G \]
where \( X \) is the analyte and \( Y \) is the only absorbing species at the wavelength under consideration. The final concentration of \( Y \) is given by
\[ c = (M_Y - rM_X)/V_T \] \[16\]
where \( M_Y \) and \( M_X \) are the millimoles of \( Y \) and \( X \) respectively, and \( V_T \) is the total volume in milliliters. If the amount of \( X \) placed in the solution in the sample beam is held at zero, then
\[ c = M_Y/V_T \] \[17\]
and
\[ c' = (M'_Y - rM'_X)/V'_T \] \[18\]
Also
\[ M_Y = c_Y V_Y \] \[19\]
where \( V_Y \) and \( c_Y \) are the volume and concentration of stock solution \( Y \) respectively. Similarly
\[ M'_Y = c'_Y V'_Y \] \[20\]
Also
\[ M'_X = c'_X V'_X \] \[21\]
where $V_Y$ is the volume of the analyte solution placed in the reference beam. Substituting equation [19] into equation [17] gives
\[ c = \frac{c_Y V_Y}{V_T} \]  
[22]
Similarly, substituting equations [20] and [21] into equation [18] gives the following:
\[ c' = \frac{(c_Y' V_Y' - r c_X' V_X')}{V_T} \]  
[23]
Substitution of equations [22] and [23] into equation [15] yields
\[ \Delta A = ab \left( \frac{(c_Y V_Y / V_T)}{(c_Y' V_Y') / V_T} - \frac{(c_X' V_X') / V_T}{V_T} \right) \]  
[24]
Since in most applications only one stock solution of $Y$ is used, $c_Y' = c_Y$.
Also the analytical procedure can easily be arranged such that the total volumes of both reference and sample beam solutions are equal. Consequently, equation [24] may be rewritten as
\[ \Delta A = ab \left\{ \frac{[c_Y (V_Y - V_Y) + r c_X V_X]}{V_T} \right\} \]  
[25]
However
\[ c_X' V_X' / V_T = [X]' \]  
[26]
where $[X]'$ is equal to the molar concentration of $X$ in the solution in the sample beam. Rearranging equation [25] and substituting equation [26] it is seen that
\[ \Delta A = ab [X]' + abc_Y (V_Y - V_Y') / V_T \]  
[27]
The effective molar absorptivity of the nonabsorbing species $X$ may be defined by
\[ ar = \epsilon_X \]  
[28]
For a given analysis the following relationship can be held constant:

\[ \frac{abc_Y}{V_T} = k \]  \[ 29 \]

where \( k \) is an experimentally determined constant.

Finally substituting equation [28] and [29] into equation [27] the following is obtained:

\[ \Delta A = \varepsilon_X b[X]' + k(V_Y - V_Y') \]  \[ 30 \]

or

\[ \Delta A = \varepsilon_X b[X]' + K(V_Y/V_Y' - 1) \]  \[ 31 \]

where \( K \) becomes \( V_Y'k \).

For the case where the initial volume of \( Y \) in both solutions is the same, equation [31] reduces to

\[ \Delta A = \varepsilon_X b[X]' \]  \[ 32 \]

which is the relationship usually employed in indirect differential spectrophotometry. It should be noted from equation [31] that a plot of \( \Delta A \) versus \( [X]' \) is a straight line and that variation of the last term should give a family of straight lines of different intercepts. Each of the straight lines in the family will possess its own optimum concentration range. Therefore, it should be possible to obtain a series of lines with overlapping optimum concentration ranges. This would provide an extended optimum concentration range with which to work.

The effects of varying the \( V_Y/V_Y' \) ratio on the optimum concentration range have been experimentally and theoretically determined. Theoretical plots are given
for $\Delta A$ versus p.p.m. cyanide ion in Figure 5, and $1 - \Delta T$ versus p.p.m. cyanide ion in Figure 6. These plots will serve for purposes of comparison with experimental plots Figures 8 and 9. The absorbing species chosen was the hypochlorite ion, which has a molar absorptivity of 347 m$^2$ cm$^{-1}$ mole$^{-1}$ when measured at 2930 Å in the pH range of 11.2 to 11.4. Two assumptions were made in constructing the theoretical plots. It was assumed the hypochlorite ion undergoes a 1:1 reaction with cyanide ion, and further that the reaction goes essentially to completion. The principle reaction is given by (21):

$$\text{CN}^- + \text{OCl}^- \rightarrow \text{OCN}^- + \text{Cl}^-$$

The cyanate and chloride ions have been shown not to exhibit significant absorption at 2930 Å (22).
Figure 5. Theoretical plots of various $V'_{y}$,$V''_{y}$ ratios applying to equation [33].
Figure 6. Theoretical Ringbom plots applying to Figure 5.
EXPERIMENTAL

Calibration Plot for Hypochlorite Ion

Standard solutions of hypochlorite were prepared from a commercial bleach solution which previously had been standardized iodometrically against a standard sodium thiosulfate solution with starch indicator.

The diluted hypochlorite solutions were buffered in the region of pH 11.2 to 11.4 with a tripotassium phosphate-dipotassium hydrogen phosphate buffer system. The absorbancy of these solutions was then measured relative to a reagent blank on a Cary Model 14 spectrophotometer. All measurements were made at 2928 Å with 1.00 cm. cells, and the corresponding absorbancy values were read directly. A typical plot of absorbancy versus concentration of hypochlorite ion may be found in Figure 7.

Indirect Differential Procedure

Reagents and solutions

Reagent grade chemicals were used unless otherwise specified and all solutions were made in distilled water.

Solution A. A 0.025 to 0.040 M stock solution of sodium hypochlorite was prepared by measuring 23 to 38 ml. of a 5.25% (W/W) commercial bleach (Roman Cleanser Bleach
or Clorox) and adjusting the pH to the range of approximately 11.2 to 11.4 with sodium hydroxide. The resulting solution was then diluted to one liter.

Concentrations of the hypochlorite stock solutions were determined spectrophotometrically according to the procedure previously given. The concentrations were read directly from a calibration plot, Figure 7. The normality of the hypochlorite stock solution was found to change significantly over relatively short periods of time. Consequently, it was necessary to standardize this reagent frequently.

Solution B. A 10% solution of dipotassium hydrogen phosphate was prepared by dissolving 100 grams of $\text{K}_2\text{HPO}_4$ and diluting to a volume of one liter.

Solution C. A 10% solution of hydrated tripotassium phosphate was prepared by dissolving 100 grams of $\text{K}_3\text{PO}_4\cdot\text{xH}_2\text{O}$ and diluting to a total volume of one liter.

Solution D. Several stock solutions of potassium cyanide in the range of 10 to 500 parts per million were prepared by dissolving appropriate amounts of fresh KCN and diluting to one liter. Precaution was taken to avoid the presence of ammonia or other oxidizable materials as these will also undergo reaction with the hypochlorite ion.

The normality of the potassium cyanide stock solution was determined argentimetrically by Denige's
Figure 7. Typical calibration plot for determining hypochlorite concentrations.
Modification (23) of the Liebig Method (24). Frequent standardizations of the cyanide solution were necessitated due to its relative instability.

Procedure

The general procedure for obtaining a plot of $\Delta A$ versus p.p.m. CN$^{-}$ for a given $V_y:V_Y$ ratio is as follows:

1. A predetermined volume of solution A was pipetted into a 100 ml. volumetric flask. To this, 5 ml. of solution B was added and mixed thoroughly. Then 10 ml. of solution C was added, and the flask diluted to volume. This solution, the reagent blank, was placed in the sample beam of a double beam spectrophotometer. The volume of solution A was chosen so as to give an absorbancy in the range of 0.5 to 1.5 relative to a distilled water reference.

2. A predetermined volume of solution A, either the same as that taken for the reagent blank or some fraction or multiple of it, was added to each of a number of 100 ml. volumetric flasks, depending upon the number of readings desired for the plot. Five milliliters of solution B was then added to each of these flasks and their contents mixed thoroughly. Then the various amounts of the cyanide stock solution, solution D, were added to the flasks. The amount of cyanide solution added to each flask was determined by the volume ratio desired. The
flasks were then shaken thoroughly, and set aside for about thirty minutes to allow for the reaction to reach completion.

Finally, 10 ml. of solution C were added to buffer the mixtures to a pH of approximately 11.2 to 11.4. The flasks were then diluted to volume and each solution in turn placed in the reference beam of a double beam spectrophotometer. The absorbance of the reagent blank relative to these solutions is in actuality the differential absorbance of these solutions.

Instrumental Parameters

A Cary Model 14 spectrophotometer was used in all the absorbance and differential absorbance measurements. These measurements were read at a wavelength setting of 2928 Å, the wavelength of maximum absorbance for the hypochlorite ion at a pH of 11.2 to 11.4. The dynode, slit control, and slit height settings were 2, 20, and 20 mm. respectively. These conditions appeared to give a reasonable signal to noise ratio. For the solutions studied, the effective slit width varied from 0.08 to 1.00 mm. giving a spectral slit width variation from 0.16 to 2.00 mm.
Statistical treatment of data

Values of $\Delta A$ which deviated significantly from the mean were tested by the method described by Dean and Dixon (25) at the 90% confidence level. The mean and standard deviation, $\sigma$, were calculated and appear in Table 2.

Resulting Plots

Two different plots were made from the data shown in Table 2. Figure 8 represents the plot of the differential absorbance versus the concentration of cyanide ion. Figure 9 represents a Ringbom plot of the data shown in Table 2. Figures 8 and 9 should be comparable to the theoretical plots, Figures 5 and 6, calculated from equation [31].
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<tr>
<td></td>
<td></td>
<td></td>
<td>2.064</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>5.160</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.32</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>15.48</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.64</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 2. Experimental Data (continued)

<table>
<thead>
<tr>
<th>Vol. Ratio</th>
<th>Initial Concentrations</th>
<th>No. of Detns.</th>
<th>Avg.</th>
<th>σ</th>
</tr>
</thead>
<tbody>
<tr>
<td>C10\textsubscript{S}:C10\textsubscript{R}</td>
<td>C10\textsuperscript{-} \textsuperscript{R} mmoles</td>
<td>C10\textsuperscript{-} \textsuperscript{S} mmoles</td>
<td>ppm. CN\textsubscript{S}</td>
<td></td>
</tr>
<tr>
<td>2:5</td>
<td>4.406</td>
<td>1.763</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>25.80</td>
<td>30.96</td>
<td>36.12</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1.482</td>
<td>0.0017</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2:5\textsuperscript{a}</td>
<td>4.406</td>
<td>1.763</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.000</td>
<td>5.160</td>
<td>10.32</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1.119</td>
<td>0.0058</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6:5</td>
<td>4.978</td>
<td>5.973</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>29.79</td>
<td>39.72</td>
<td>49.65</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1.250</td>
<td>0.0231</td>
<td></td>
<td></td>
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<tr>
<td>6:5\textsuperscript{b}</td>
<td>4.978</td>
<td>5.973</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>29.79</td>
<td>39.72</td>
<td>59.58</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.241</td>
<td>0.0171</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Only five minutes were allowed for the reaction of A and B with solution D before adding C, and measuring.

\textsuperscript{b} Solution D was added to a mixture of A, B, and C. It was allowed about thirty seconds to react before diluting, and measuring.
Figure 8. Experimental plots of various $V_{14}/V_{15}$ ratios applying to equation (33).
Figure 9. Experimental Ringboom plots applying to Figure 8.
CONCLUSIONS

Interpretation of Data

A comparison of the experimental data as represented by the plots of Figure 8 with the theoretical plots of Figure 5 reveals a close resemblance between the plots of the two figures except for the experimental plots labeled 2:5 and 6:5. The intercepts with the ordinates do not agree due to the different concentrations of hypochlorite ion used in the experimental work as compared with the concentrations used in the theoretical calculations. The discrepancies in the case of the 2:5 and 6:5 lines will be explained in more detail.

A similar agreement can be noticed by comparison of Figures 9 and 6 of the experimental and theoretical Ringbom plots respectively.

An inspection of the Ringbom plots of Figure 6 reveals an advantage of the indirect differential method. A projection of the linear portions of the individual curves, on the abscissa, shows that there is an overlap of individual optimum concentration ranges. This overlap is an indication that the optimum concentration range has been demonstrated, by the experimental work, to be expanded. A judicious choice of the ratios $V_Y:V_Y^*$ may allow an analysis to be performed in an optimum region.
However it should be noted that this expansion is handi-
capped in the upper and lower limits of concentration.

The plot 6:5 of Figure 9 represents a sample
solution, initially enriched with the absorbing species
relative to the reference solution. The linear portion
of this plot is in the high concentration region of
cyanide ion. In this region the curve has a steep slope
where a relatively large differential absorptance
\((1 - \Delta T)\) is observed for a small change in the cyanide
ion concentration. This is a desirable feature with
respect to sensitivity, however the narrow range of
concentration covered by this linear portion of the
curve is not suitable from a practical point of view.
On the other hand due to the nonlinearity of the Ringbom
plot, such plots are seldom used as working curves.

At the low concentration limit, represented by the
3:5 plot in Figure 9, the linear portion of the plot is
of a very small slope. As a result the slight change in
the differential absorptance with the concentration
change limits the applicability of the method in the low
concentration region.

Volume ratios of 3:5 and 2:5 in Figures 8 and 9,
while not producing large changes of differential
absorptance per unit change of cyanide concentration, do
give rise to large \(\Delta A\) and \(1 - \Delta T\) values. For example
at 45.76 p.p.m. \(\text{CN}^-\) and a volume ratio of 3:5 a
differential absorbance of 1.241 corresponding to a differential absorptance of 0.943 is observed. With a single beam spectrophotometer, this has the additional disadvantage of giving a transmittance which is not near its region of minimum concentration error. This is not nearly as great a disadvantage for most double beam, absorbance recording, spectrophotometers, which have a minimum error corresponding to absorbances between 0.4 and 1.4 absorbance units.

To illustrate the trends in the experimental data more fully, the data of Table 2 has been retabulated in Table 3 to show the dependence of the relative standard deviation upon the volume ratio and the concentration of cyanide ion. It should be noted that for low cyanide ion concentrations, the relative precision of measurement increases as the volume of absorbing species in the sample solution decreases with respect to that in the reference solution. This was to be expected due to the location of the linear portion of the Ringbom plots as noted above. To determine intermediate amounts of cyanide ion, the best precision would be obtained when the volume of absorbing species in the sample and reference solutions is more nearly equal.
Table 3. Relative standard deviation as a function of volume ratio and cyanide concentration

<table>
<thead>
<tr>
<th>Volume Ratio</th>
<th>ppm. CN⁻</th>
<th>ΔA</th>
<th>σ⁻</th>
<th>100σ⁻/ΔA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>1.03</td>
<td>0.008</td>
<td>0.003</td>
<td>37.5</td>
</tr>
<tr>
<td>4:5</td>
<td>1.03</td>
<td>0.300</td>
<td>0.004</td>
<td>1.3</td>
</tr>
<tr>
<td>3:5</td>
<td>1.02</td>
<td>0.602</td>
<td>0.005</td>
<td>0.83</td>
</tr>
<tr>
<td>2:5</td>
<td>1.03</td>
<td>0.932</td>
<td>0.001</td>
<td>0.10</td>
</tr>
<tr>
<td>1:1</td>
<td>5.17</td>
<td>0.070</td>
<td>0.003</td>
<td>4.30</td>
</tr>
<tr>
<td>4:5</td>
<td>5.17</td>
<td>0.365</td>
<td>0.003</td>
<td>0.83</td>
</tr>
<tr>
<td>3:5</td>
<td>5.09</td>
<td>0.667</td>
<td>0.003</td>
<td>0.45</td>
</tr>
<tr>
<td>2:5</td>
<td>5.16</td>
<td>1.088</td>
<td>0.001</td>
<td>0.092</td>
</tr>
<tr>
<td>1:1</td>
<td>15.53</td>
<td>0.217</td>
<td>0.002</td>
<td>0.92</td>
</tr>
<tr>
<td>4:5</td>
<td>15.50</td>
<td>0.497</td>
<td>0.003</td>
<td>0.60</td>
</tr>
<tr>
<td>3:5</td>
<td>15.26</td>
<td>0.811</td>
<td>0.002</td>
<td>0.25</td>
</tr>
<tr>
<td>2:5</td>
<td>15.48</td>
<td>1.450</td>
<td>0.007</td>
<td>0.48</td>
</tr>
<tr>
<td>1:1</td>
<td>25.88</td>
<td>0.361</td>
<td>0.007</td>
<td>1.94</td>
</tr>
<tr>
<td>4:5</td>
<td>25.82</td>
<td>0.646</td>
<td>0.005</td>
<td>0.77</td>
</tr>
<tr>
<td>3:5</td>
<td>25.43</td>
<td>0.949</td>
<td>0.002</td>
<td>0.21</td>
</tr>
<tr>
<td>2:5</td>
<td>25.80</td>
<td>1.481</td>
<td>0.001</td>
<td>0.067</td>
</tr>
<tr>
<td>6:5</td>
<td>39.72</td>
<td>0.343</td>
<td>0.004</td>
<td>1.17</td>
</tr>
<tr>
<td>1:1</td>
<td>33.00</td>
<td>0.458</td>
<td>0.007</td>
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<td>4:5</td>
<td>36.16</td>
<td>0.780</td>
<td>0.002</td>
<td>0.25</td>
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<td>3:5</td>
<td>35.60</td>
<td>1.100</td>
<td>0.003</td>
<td>0.27</td>
</tr>
<tr>
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<td>36.62</td>
<td>1.481</td>
<td>0.002</td>
<td>0.13</td>
</tr>
<tr>
<td>6:5</td>
<td>49.65</td>
<td>1.064</td>
<td>0.0496</td>
<td>4.66</td>
</tr>
<tr>
<td>1:1</td>
<td>51.75</td>
<td>0.709</td>
<td>0.0013</td>
<td>0.083</td>
</tr>
<tr>
<td>4:5</td>
<td>51.65</td>
<td>0.999</td>
<td>0.0026</td>
<td>0.026</td>
</tr>
<tr>
<td>3:5</td>
<td>50.85</td>
<td>1.283</td>
<td>0.0014</td>
<td>0.11</td>
</tr>
<tr>
<td>2:5</td>
<td>51.60</td>
<td>1.482</td>
<td>0.0009</td>
<td>0.061</td>
</tr>
</tbody>
</table>

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The discrepancies of lines 2:5 and 6:5 in Figure 8 which represent small and large volume ratios (Vy:V£) respectively may be explained by the following:

(1) Line 2:5 of low volume ratio:

The main feature of this curve is that it levels off in the high concentration region of cyanide ion. In this horizontal portion of the curve it is assumed that the absorbing species, hypochlorite ion, has been consumed. The absorbance of the sample solution does not change with increased cyanide ion concentration. Thus the observed absorbance is due to the reference solution. A deficiency in the concentration of hypochlorite ion may result in an incomplete reaction. An invariant slope with a change in the concentration of cyanide ion supports this assumption. The optimum concentration of the oxidizing agent, hypochlorite ion, required for a complete reaction may be determined by a series of experiments using different concentrations of hypochlorite ion. By such experiments one may be able to determine such an optimum concentration before which a leveling off can be observed. In this work, such experiments were not performed since the corresponding lines lie sufficiently close to one another as to render additional measurements unnecessary.
(2) Line 6:5 of high volume ratio:

The discrepancy in this case cannot be explained by the same arguments without contradiction. However, a possible explanation may be sought by assuming the presence of side reaction(s) taking place sequentially with the principle reaction. The assumed reaction may consume hypochlorite ion. This will produce a larger $\Delta A$ which is in agreement with the observations as shown in Figure 8. The observed discrepancy was reduced by allowing a very short time between mixing and measurement steps as seen in plot 6:5b. It is believed that such an improvement is due to a side-reaction with a slower reaction rate than the principle one. A possible reaction sequence for the side-reaction may be as:

$$3 \text{CN}^- + 3 \text{ClO}_3^- \rightarrow 3 \text{OCN}^- + 3 \text{Cl}^- \quad [33]$$

$$3 \text{OCN}^- + 3 \text{H}_2\text{O} \rightarrow \text{I} + 3 \text{OH}^- \quad [34]$$

$$\text{I} + 3 \text{ClO}_3^- \rightarrow \text{II} + 3 \text{OH}^- \quad [35]$$
The overall stoichiometry of reactions [33], [34], and [35] indicate that two moles of hypochlorite ion would react per mole of cyanide ion. This would mean that the slope of the line obtained in a plot such as 6:5 of Figure 8 should be double that of the normal line in the family.

The line obtained for the 6:5 ratio of hypochlorite ion in the sample to the reference solution has a slope which initially approaches twice that of the expected line in the family. It will be noted that with a larger cyanide ion concentration the line tends to level off. All the measurements represented by this curve were found to be time dependent, thus making interpretation difficult. Nevertheless, the overall rate of reaction [34] could be highly dependent upon the hypochlorite ion concentration. If this were the case, it would not be unreasonable to anticipate a leveling effect for the 6:5 line in Figure 8 at higher cyanide concentrations since the excess of hypochlorite ion is becoming smaller, thereby causing the reaction to proceed at a slower rate.

The specific reactions shown in equations [34], and [35] have not as yet been substantiated. Reactions similar to equation [34] are known to occur with organic cyanates and isocyanates (26, 27). The intermediate, I, is named cyanuric acid or isocyanuric acid, s-triazine-2,4,6 (1H,3H,5H) trione. Also reactions similar to
equation [35] have been reported (28, 29).

A plot of absorbance versus the molar concentration ratio of cyanide ion to hypochlorite ion should reveal the overall reaction stoichiometry from the extrapolated ordinate intercepts, Figure 10. Due to the slowness of the reaction, an appreciable degree of uncertainty of the points may be present and consequently a definite interpretation could not be made. Nevertheless, it would seem that some significance might be attached to the fact that the abscissa intercepts are in the approximate region of a 1:2 stoichiometry. Such an interpretation would tend to support the reaction sequence given in equations [33], [34], and [35].

An attempt was made to determine the presence of the products of the side reactions polarographically but no conclusive results were obtained. Anodic current-voltage curves of a cyanide solution revealed two oxidations. These would correspond to the oxidation of cyanide ion and water. When cyanate ion was determined anodically, only the oxidative wave for water was obtained. While such data do not necessarily show what the reaction products of the hypochlorite-cyanide reaction are, it should be pointed out that the observed polarographic data was not inconsistent with the postulated reaction products. Chlorocyanurate, II, was determined cathodically, but a usable curve was not obtained, possibly due
Figure 10. Stoichiometry plots. The molar concentrations of hypochlorite ion used were: 1, 1.77 × 10^{-3} M; 2, 2.66 × 10^{-3} M; 3, 3.10 × 10^{-3} M; 4, 3.54 × 10^{-3} M; 5, 4.65 × 10^{-3} M; and 6, 3.86 × 10^{-2} M.
to depolarization of the dropping mercury electrode by a chlorine (I) species.

Attempts were made to crystallize some of the suspected products in order to run a qualitative test for cyanuric acid (30). It was not possible to isolate sufficient material to obtain a qualitative test or an infrared spectrum. Analysis by nuclear magnetic resonance was not possible due to the presence of excess hypochlorite ion which is not easily removed.

Difficulties in establishing the identity of the reaction products result from the very low concentrations being used. The formation of chlorocyanurate, II, which has been proposed would be in extremely small amounts. Scaling up the reaction was considered, however this was not done because reaction conditions could have been significantly different from those of the system under consideration.

Proposals for Further Work

It is apparent that the reactions of hypochlorite ion are still not fully understood. An exploration of such a system is desirable. The feasibility of scale expansion to work in the optimum concentration range has been demonstrated. This might have been better illustrated, if it were not for the limitations of the chemical system chosen in this work. It is suggested
that a more stable chemical system be chosen to better demonstrate the usefulness of the technique. A series of stable dye solutions, colored filters, or neutral density filters could be used in place of a chemical reaction system to substantiate the scale expansion technique.

The method has several features which may be used to minimize errors. Stray radiation and slit width errors may be decreased by choosing a more suitable concentration ratio at which to carry out the analysis. Temperature effects are reduced by the differential measurement. The method also offers the advantages of the use of precision methods, molar amplification, specificity, the use of unstable chromophores, replacing the parameters of one absorbing species with those of another, and the use of reagents which are not highly purified. In addition, there is the prospect of scale expansion and choice of an optimum concentration range. The indirect differential method should prove very helpful for analyses where a high degree of precision is required.
REFERENCES


VITA

The author was born in Detroit, Michigan on January 31, 1943. He received his grade school training in Detroit. He attended South Lake Junior High School in St. Clair Shores, Michigan. The author graduated from Clintondale High School in Mt. Clemens, Michigan in 1960. He enrolled at Wayne State University in Detroit, Michigan in the fall of 1960 and majored in chemistry. He received the degree of Bachelor of Science in Chemistry in 1965. Work was started on a Master's degree at Western Michigan University, Kalamazoo, Michigan in the fall of 1965. This thesis concludes the author's work on the Master of Arts Degree.

The author is married.