ANALYSIS OF CHLORINE AND CHLORAMINE

IN A NATURAL WATER SYSTEM

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PREFACE

The objectives of this study were to develop an analytical pro-

cedure for and study the effect of chlorine and chloramine in a natural

water system.

Dr. Louis P. Varga served as major advisor. The other members of

the advisory committee include Drs. Harry Gearhart and Anthony Gaudy.

I am grateful for the kind assistance of these and many other faculty

and colleagues.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Bacteria and algae that are present in natural waters must not be allowed to grow in the cooling systems of electrical power plants since they would seriously impede heat transfer and water flow. One of the common methods of defouling is the addition of chlorine to the cooling system. Chlorination is effective for defouling but also may cause injury to plant and animal life in the body of water that receives the effluent from the power plant. As a result the residual chlorine entering the environment should be controlled so that the environment is exposed to as small a risk of injury as possible.

The duration, frequency and amount of chlorination to prevent fouling varies from location to location. A common practice in the United States is to use two injections a day of 3.0 mg/l for 15 minutes each (1). Continuous addition of 0.02 to 0.05 mg/l is used in coastal power stations in Great Britain (2). Addition of 2.0 to 3.0 mg/l of chlorine for a two-hour period once a day has also been used (3). Regardless of which method is used a residual level of 0.5 ppm available chlorine must be produced to effectively defoul the system (4).

In order to minimize the effects on the environment extensive research must be done to characterize the effect of chlorine on natural water systems. Complicating this effort is the presence of ammonia in natural waters as a part of the nitrogen cycle. (See Figure 1.)
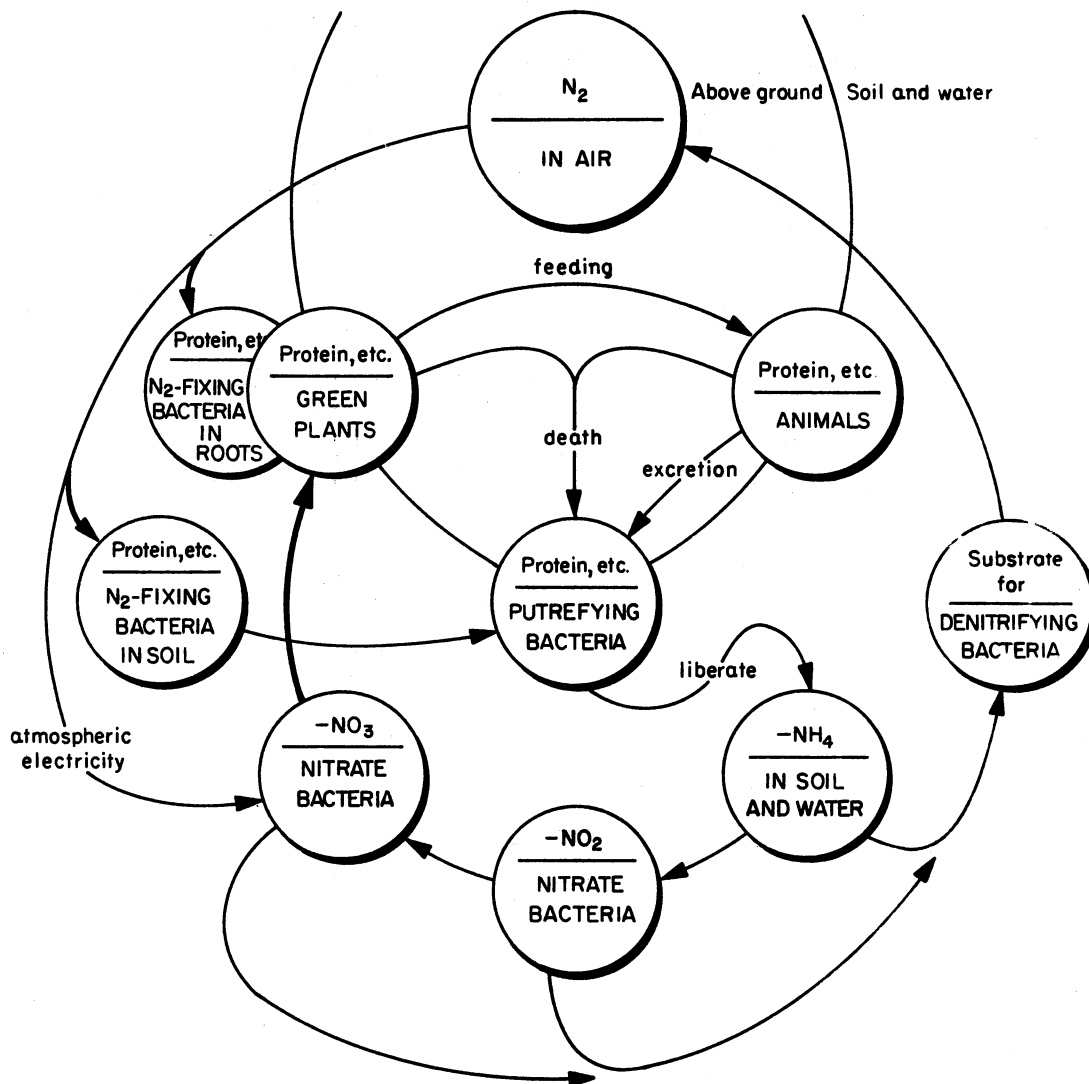
Figure 1. Nitrogen Cycle (5)

Chlorine in the presence of ammonia forms chloramines whose toxicity is different from free chlorine.

The difference in toxicity of free chlorine and chloramine makes it necessary to measure or calculate the concentrations of these species in order to characterize their individual effect on an aquatic environment. Chlorine and chloramine establish an equilibria system which must be modeled to permit calculation of the chlorine and chloramine species present. The aid of a computer is necessary to perform the complex computation resulting from the equilibria model. A computer program designed to solve multiple simultaneous equations is required in order to describe the system.

Chlorine - Chloramine Equilibria

In an ammonia-water-chlorine system six chlorine containing species excluding chloride ion and hydrochloric acid may be present. These are molecular chlorine (Cl_2), hypochlorus acid (HOCl), hypochlorite ion (OCl^-), monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and nitrogen trichloride (NCl_3). The latter five are of interest because of their ability to oxidize other compounds. This oxidation potential gives these species their germicidal characteristics (6).

The concentration of each species present depends upon the chemical equilibria, pH, temperature and reactant concentrations. (Note: All equilibrium constants given are for $25^{\circ}C$.) Molecular chlorine undergoes a disproportionation reaction in water to establish an equilibrium with hypochlorous acid and hydrochloric acid as given below (7):

$$Cl_2 + H_2O \rightleftharpoons HOCl + Cl^- + H^+, \quad k_1 = 3.94 \times 10^{-4} \tag{1}$$
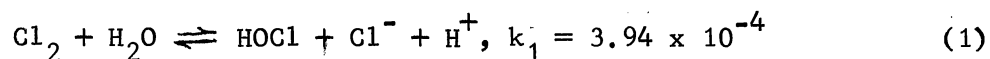
The hydrolysis is virtually complete and the concentration of Cl_2 is negligible at a pH greater than 3 or total chlorine concentrations of less than 1000 ppm (7). Hypochlorous acid partially ionizes according to Equation 2 (7).

$$HOCl \rightleftharpoons H^+ + OCl^-, \quad k_2 = 3.2 \times 10^{-8} \tag{2}$$
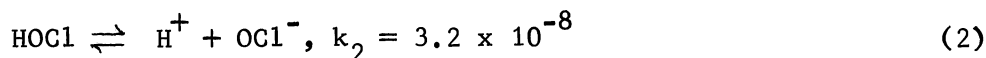
Monochloramine and dichloramine establish an equilibrium given by Equation 3 (8).

$$2NH_2Cl + H^+ \rightleftharpoons NH_4^+ + NHCl_2, \quad k_3 = 6.7 \times 10^5 \tag{3}$$
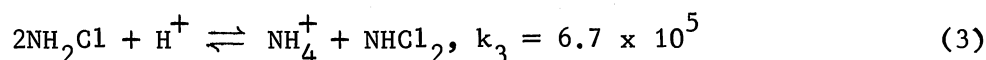
The equilibria between ammonia, water and the various chlorine containing species are given by the following equations (9, 10, 4):

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-, \quad k_4 = 1.81 \times 10^{-5} \tag{4}$$

$$NH_3 + HOCl \rightleftharpoons NH_2Cl + H_2O, \quad k_5 = 3.6 \times 10^9 \tag{5}$$

$$NH_2Cl + HOCl \rightleftharpoons NHCl_2 + H_2O, \quad k_6 = \frac{k_5 k_3 k_w}{k_4} = 1.33 \times 10^6 \tag{6}$$
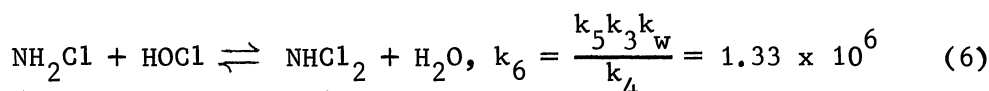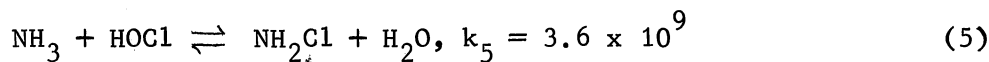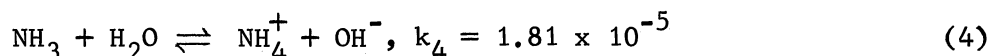
(Note: k_w equals the ionization constant of water.)

$$NHCl_2 + HOCl \rightleftharpoons NCl_3 + H_2O, \quad k_7 \text{ unavailable} \tag{7}$$
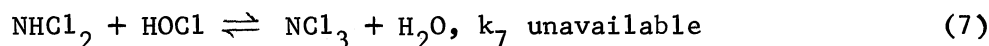
Even though k_7 is undetermined it is of little consequence in chlorination of natural waters because NCl_3 is known to exist only in aqueous solutions at pH values less than 4 (11).

The rate of conversion of Equation 5 is pH sensitive. The fastest conversion of HOCl to NH_2Cl occurs at pH 8.3 (6). Table I gives the time required to convert 99% of a $0.2 \times 10^{-3} \underline{M}$ HOCl to NH_2Cl in a $1.0 \times 10^{-3} \underline{M}$ ammonia solution at $25^{\circ}C$.

TABLE I

TIME REQUIRED FOR CONVERSION OF HOCl TO NH_2Cl

pH	Seconds
2	421
4	147
7	0.2
8.3	0.069
12	33.2

The further disproportionation of ClO^- to ClO_3^- is possible (12).

$$3ClO^- \rightleftharpoons 2Cl^- + ClO_3^-, \text{ k } 10^{27} \tag{8}$$
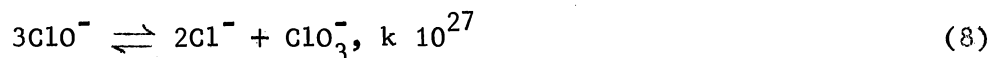
A significant loss of ClO^- due to Equation 8 is discounted by prior investigators, Draley (4) and Jolley (13).

Chemical Decomposition of Chlorine

Breakpoint Reaction

As the ratio of total initial chlorine to total initial ammonia is increased a sudden loss of residual chlorine occurs with a simultaneous loss of ammonia. Additional excess chlorine results in a recovery of residual chlorine. This phenomenon known as the "breakpoint" reaction was reported by Griffin (14) in 1939.

This phenomenon is illustrated in Figure 2 (15). The reactions which cause this phenomenon occur most rapidly in the pH range of 7 to 8 (14). The relative minima occurs at an approximate weight ratio of chlorine to ammonia nitrogen of 10:1 (6). The details of this reaction
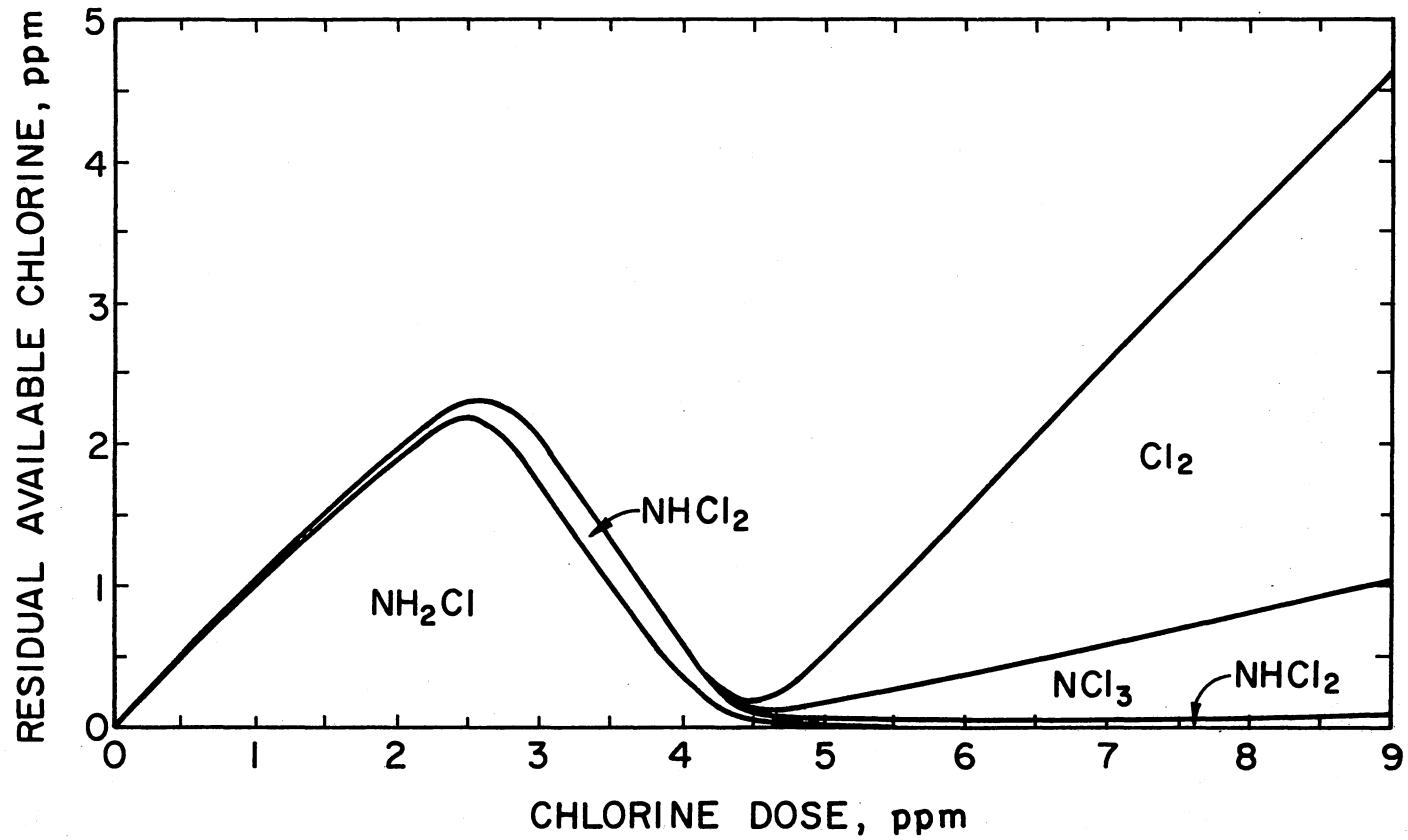
-Chlorine Dose-Residual Curve at pH 7.3-7.5 after 2 hours' contact. Initial Ammonia - 0.5 ppm (N)

Figure 2. Breakpoint Reaction (15)

are not fully understood but the process may be approximated by Equation 9 (4, 13).

$$NH_2Cl + NHCl_2 + HOCl \rightleftharpoons NO_2 + 4H^+ + 4Cl^- \qquad (9)$$
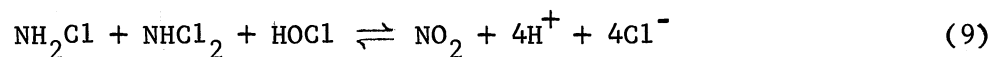
The rate of the breakpoint reaction depends upon the ammonia nitrogen level. The range is from a few minutes for 30 ppm ammonia nitrogen to approximately one-half hour for ammonia nitrogen level below one ppm (4).

Photo Decomposition

Hypochlorous acid decomposes to form oxygen in a reaction catalyzed by ultraviolet radiation (6).

$$HOCl \rightleftharpoons 1/2\ O_2 + H^+ + Cl^- \qquad (10)$$

The reaction rate depends upon the concentration of HOCl and OCl$^-$ and on the radiation intensity. Reaction rates in the light vary from 50 to 200 times faster than the rate in the dark.

Methods of Analysis

Most methods for the determination of free or combined chlorine are based on reactions with nonspecific reducing agents. Definite test conditions can achieve specificity for the chlorine containing species.

The iodometric method is considered the method against which other methods are compared. It is suitable for determining high chlorine residuals. However, the method is not accurate below chlorine concentrations of 1 mg/1 (16).

The amperometric titration method is one of the most accurate for

the determination of free and combined chlorine. Common oxidizing agents, temperature variations and color do not interfere as in other methods (17).

The orthotolidine methods have been used widely in water plant control applications. The orthotolidine-arsenite method measures free and combined chlorine separately (16).

The ferrous DPD method (18), the methyl orange (19), and the stabilized neutral orthotolidine (SNORT) methods (20) also differentiate between free and combined chlorine residuals. The SNORT and amperometric methods also can estimate the mono- and dichloramine fractions.

The reagent for the syrinaldazine method is sensitive to hypochlorite or free chlorine but is insensitive to bound chlorine such as chloramines. The developing color follows Beer's law with only a slight deviation at the origin (21).

All methods suffer from interferences from free halogens other than chlorine and from chlorine dioxide. However, these substances are seldom present in significant quantities.

Objectives of the Investigation

The development of a computer program to calculate all of the chlorine, chloramine and ammonia species present in a natural water sample after specific species are determined by one of the standard methods for analysis of chlorine is necessary. This program must be able to solve multiple simultaneous equations resulting from the equilibria equations given in Equations 1 through 6. A check of the ability of the equilibria model to predict chlorine species under conditions similar to those in natural waters is also required.

The application of this model of chlorine containing species to characterize the effects of chlorine on algae growth would contribute to the understanding of the effect of chlorine on an aquatic environment. The change in growth rate of the algae as measured by nitrate uptake is a useful measure of the effect of chlorine on the algae (22, 23, 24).

CHAPTER II

SOLVING CHLORINE-CHLORAMINE EQUILIBRIUM

SYSTEM BY USE OF A COMPUTER PROGRAM

The approach taken by this program is to solve (n) algebraic equations in (n) unknowns by guessing values intentionally smaller than the true value for two of the variables (25). The remaining variables are then calculated using (n-2) of the equations. The equations are sequences in such a manner that all variables are computed using the guessed variables or variables already computed in the sequence. The remaining two equations are used as test equations. If both are satisfied when all the variables are substituted into them, the problem is solved. If they are not satisfied, the master variables are systematically varied until the two test equations are satisfied.

The guessed variables, CX and CY(I), are varied in the following manner. CX is given a guessed value and two CY(I) values, CY(1) and CY(2), are found. Each CY(I) value satisfies its respective test equation. If the correct CX value has not been used, CY(1) will not equal CY(2). CX is then varied by a systematic procedure and new CY(I) values are obtained. This procedure continues until CY(1) equals CY(2). A flow chart of this procedure is given in Figure 3.

In the application of this program CX equals HOCl concentration and CY(I) equals NH_2Cl concentration. The test equations are mass balance equations for chlorine and ammonia-nitrogen. The (n-2) equations
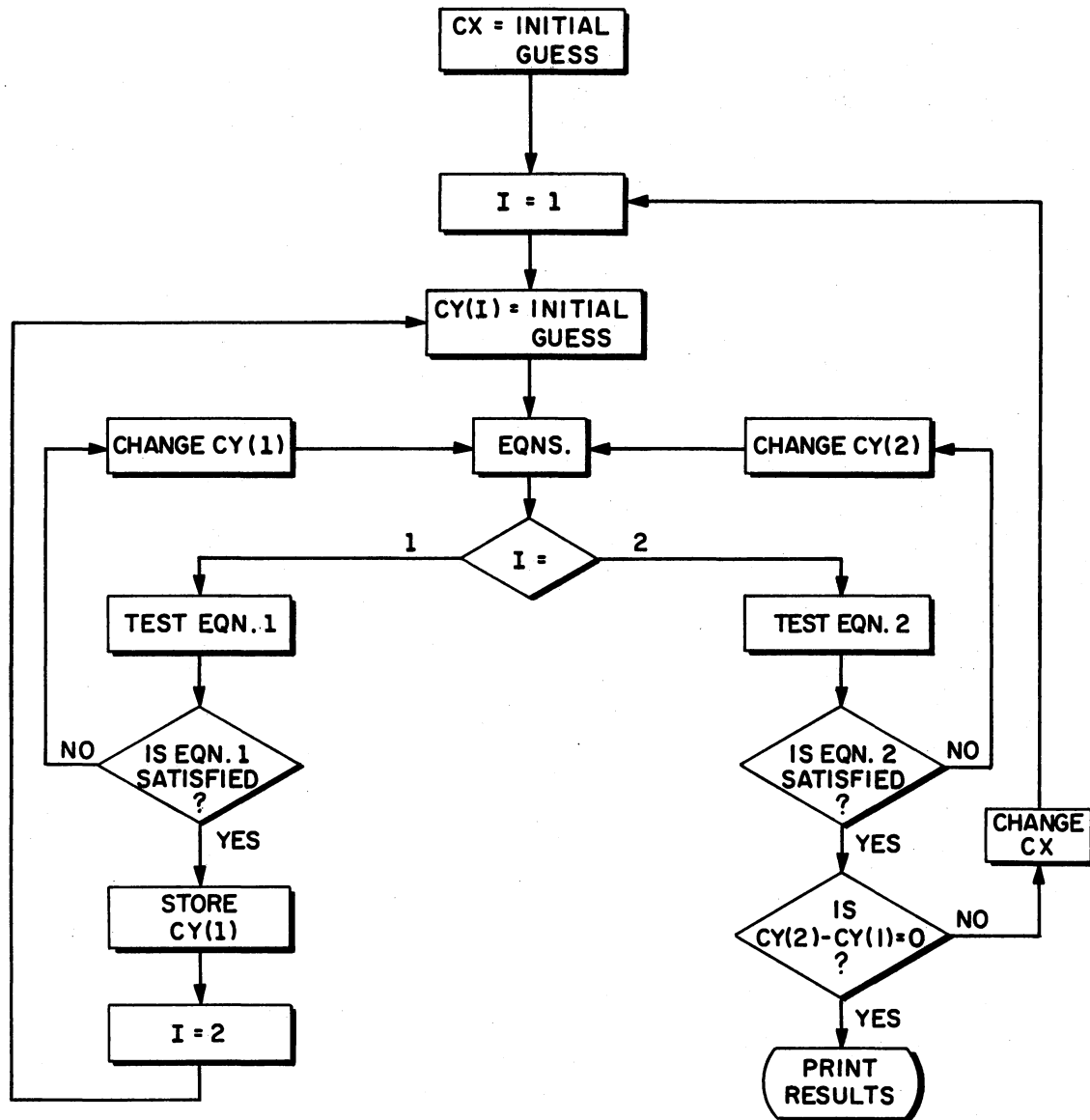
Figure 3. Flow Chart of Computer Program for Chlorine and Chloramine
Equilibrium (25)

are from the equilibrium expressions. These equations are given in Figure 4.

The variables chosen as CX and CY(I) are those which appear most often in the equations. The selection of initial values for CX and CY(I) must be smaller than the correct values. The convergence upon the correct values is illustrated by Figure 5. CY(1) and CY(2) are plotted against CX. The intersection represents the correct values for CY(I) and CX. "Y," CY(2) minus CY(1), is negative to the left of the intersection and is positive to the right of the intersection point. The sign of Y is used as the signal as to whether increase or decrease CX. Care must be taken when CX is guessed extremely small so that the initial CY(I) does not lie above one of the CY(I) lines. The limit of significant figures the computer can restrain makes the use of an equation that calculates a variable from the difference of two very similar variables an unwise choice. However, such equations can be used as test equations. A full listing of the program is given in Appendix A.

The following is a description of the flow of the program. First, the input data are read. Initial CX and CY(I) are set. Values for the concentrations for the remaining variables are calculated using the (n-2) set of equations. JY is increased by one every time CY(I) is increased. When JY = 100, search for CY(I) is terminated to prevent wasting time on the computer if errors occur. Search for CY(1) uses the sign of the difference in the two sides of Test Equation 1 as the signal to increase or decrease CY(1). Since CY(1) is too small the first time, whenever the difference is the same sign as the first CY(1) is increased. When Y, the difference, is of opposite sign to the first Y, CY(1) is decreased. When Y = 0, a search for CY(2) is begun using the same

Equilibrium equations:

$$k_w = 1.0 \times 10^{-14} = [H^+][OH^-]$$

$$k_2 = 3.94 \times 10^{-4} = [HOCl][H^+][Cl^-]/[Cl_2]$$

$$k_3 = 3.2 \times 10^{-8} = [H^+][OCl^-]/[HOCl]$$

$$k_4 = 1.8 \times 10^{-5} = [NH_4^+][OH^-]/[NH_3]$$

$$k_5 = 3.6 \times 10^{9} = [NH_2Cl]/[NH_3][HOCl]$$

$$k_6 = 1.33 \times 10^{6} = [NHCl_2]/[NH_2Cl][HOCl]$$

(Equilibrium constants from Ref. 4.)

The overall reaction can be written as:

$$Cl_2 + H_2O + NH_3 \rightleftharpoons HOCl + OCl^- + NH_2Cl + NHCl_2 + H^+ + Cl^-$$
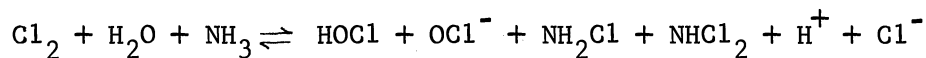
The number of electrons gained must equal the number of electrons lost,

therefore:

$$[Cl^-] \text{ produced by} = [HOCl] + [OCl^-] + [NH_2Cl] + 2[NHCl_2]$$
the reaction

By adding ambient chloride to both sides,

Total $[Cl^-] = [HOCl] + [OCl^-] + [NH_2Cl] + 2[NHCl_2] +$ ambient $[Cl^-]$

Chlorine mass balance equation:

Total chlorine $= [HOCl] + [OCl^-] + 2[Cl_2] + [NH_2Cl] + 2[NHCl_2] + [Cl^-]$

Ammonia mass balance equation:

Total $NH_3 = [NH_3] + [NH_4^+] + [NH_2Cl] + [NHCl_2]$

Figure 4.   Equations for Chlorine - Chloramine Equilibrium
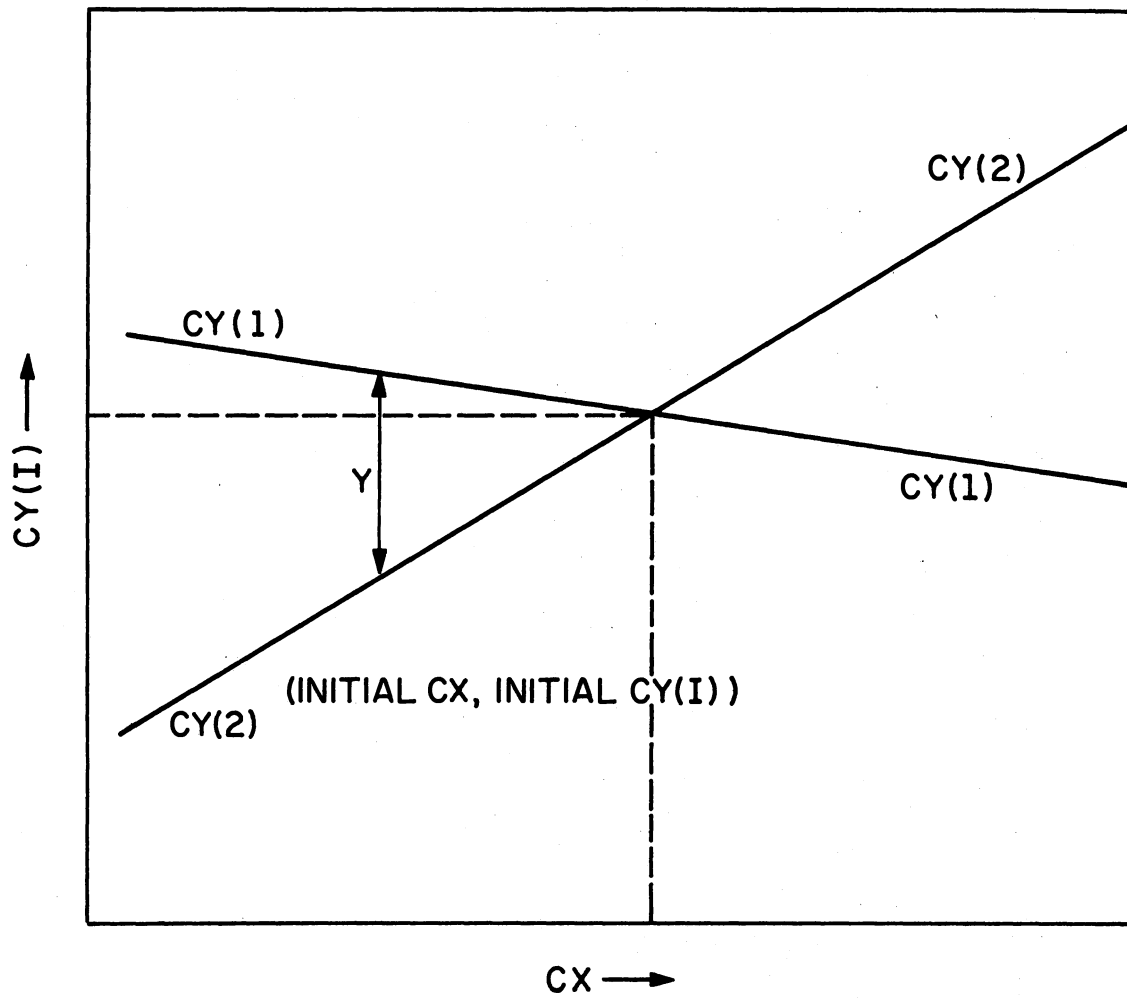
Figure 5. Convergence Upon Correct Values of CY(I) and CX (25)

process. When CY(2) is determined using Test Equation 2, CY(1) and

CY(2) are compared. If they are equal the proper CX was used, if not

CX is changed and new CY(I) values are determined. The sign of Y where

Y = CY(2) - CY(1) serves as the signal to increase or decrease CX just

as for CY(I). Search for CX is terminated after five significant fig-

ures are obtained. The results are printed and the nest data card is

read and the process begins anew.

CHAPTER III

EXPERIMENTAL ACTIVITY

Two main types of experiments were conducted in this investigation. Field experiments were conducted using lake water samples from Lake Carl Blackwell near Stillwater, Oklahoma. Laboratory experiments were conducted on algae cultures to evaluate the analytical techniques.

Field Experiments

Experimental Procedure

Samples of lake water were treated with spikes containing ^{15}N nitrate or ammonia and chlorine in a manner similar to that given by Toetz, Varga and Loughran (22). Polypropylene carboys were filled with lake water and brought to shore. Eight hundred ml of sample water was transferred into quart bottles to which the spikes were added. The bottles were agitated to achieve mixing and placed in incubation racks made of 1.25 cm steel rods. The bottles were returned to the lake and incubated at the surface from a float for a 24-hour period. pH measurements of the lake water were taken before and after the incubation period using an Orion 407 pH meter. After incubation the racks containing the bottles were brought to shore and poisoned with 10 ml Lugol's solution. Every effort was made to prevent exposure of the bottles to direct sunlight from the time of the addition of the spike until the Lugol's solution was added.

The bottles were transported to Stillwater where the contents were filtered onto Reeve Angel 984 H Ultra Glass filters using Millipore filtering apparatus. Filtering was accomplished within 48 hours after the end of the experiment.

The nitrogen containing compounds on the glass filters were converted to N_2 gas using a Coleman Nitrogen Analyzer Model 29A. The transfer of the N_2 gas into breakseal ampoules was accomplished by a semi-automatic Toeppler pump using a 4PDT relay (Potter and Brumfield, KB17AY) which controlled two solenoid valves (ASCO, Cat. No. 82602). Mercury contacts activate the relay which opens the pump alternately to the atmosphere and to a vacuum system through the solenoid valves to cycle the Toeppler (23). The Toeppler system was made and installed by Mr. Michael Pierce, a coworker in the research group. Combustion of samples was accomplished by a continuous operation with members of the team divided into two-man teams and working in shifts.

The percent ^{15}N in the algae was determined by mass spectra analysis of the gas by a CEC 21-110 B mass spectrometer. All of the gas samples were run on the mass spectrometer by Mr. Pierce, who also read all of the strip charts.

Excess lake water was collected for ambient nitrate and ammonia analysis. Nitrate levels were determined by reduction of nitrate to nitrite followed by an Azo method for the nitrite (26, 27). Ambient ammonia was determined by the phenolhydrochlorite method (28). These analyses were performed by Mr. Wesley Sallee, project technician.

The chlorine solutions used in the spikes were standardized using the iodometric method. Residual free chlorine present after the incubation period was determined by the syringaldazine method.

Chlorine Analytical Methods

Iodometric Standardization of Chlorine Solutions (16). Chlorine liberates free iodine from potassium iodide solution at pH levels below eight. Standardized sodium thiosulfate was used to titrate the free iodine. Starch was used as the indicator.

A 0.1 $\underline{N}$ solution of sodium thiosulfate was standardized using a 0.1000 $\underline{N}$ solution of $K_2Cr_2O_7$ prepared from 4.904 g of anhydrous potassium dichromate in 1,000 ml of water. Five ml of acetic acid and one g KI were added to the sample. Then the titration with sodium thiosulfate was made.

Free Residual Chlorine Determination (21). The syringaldazine reagent was prepared from syringaldehyde (Aldrich). 3.6 g of syring-aldehyde were dissolved in 50 ml of methanol. Two hundred ml of 0.1 $\underline{N}$ NaOH were added, developing a pale yellow solution. 1.05 g of hydra-zinedihydrochloride dissolved in 50 ml of distilled water was added with stirring. Stirring was continued for two hours. (Crystals began to form after approximately five minutes.) The product was suction filtered and the precipitate redissolved in 400 ml of hot ethanol. As the solution cooled the crystals reappeared. The precipitate was filtered, air-dried then placed in an oven at $50^\circ C$ over night. A 0.1% solution was prepared by dissolving 100 mg of the precipitate in hot reagent alcohol containing 90% ethanol, 5% methanol and 5% isopropanol.

A fresh working solution was prepared daily, by placing 8.0 ml of 0.1% syringaldazine solution in 15 ml of reagent alcohol. Fifty ml of pH 7 buffer (pHydrion) was added and the volume brought to 100 ml with alcohol.

A set of standard chlorine solutions was made by dilution of a standardized chlorine solution to produce a calibration curve by measuring the absorption of 530 nm radiation. Determinations of the unknown samples were then made. A Beckman DB spectrometer was used for these determinations. The chlorine solution was standardized by the iodometric method. Then the standard solution was diluted by placing 0.50 ml, 1.00 ml, 3.00 ml and 5.00 ml of the solution by using the appropriate transfer pipette into a set of 250 ml volumetric flasks and diluting to the mark with distilled water. An example of a typical calibration curve is given in Figure 6. Determinations of the unknown samples were then made. A Beckman DB spectrometer was used for these determinations.

The oxidation of syringaldazine by chlorine may be represented as follows:
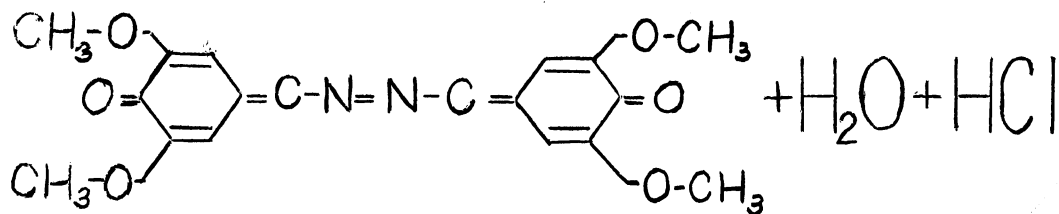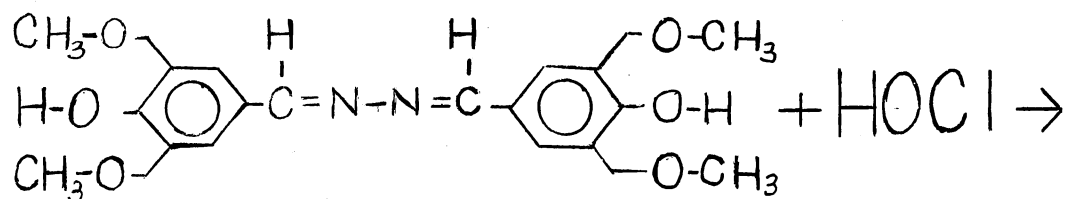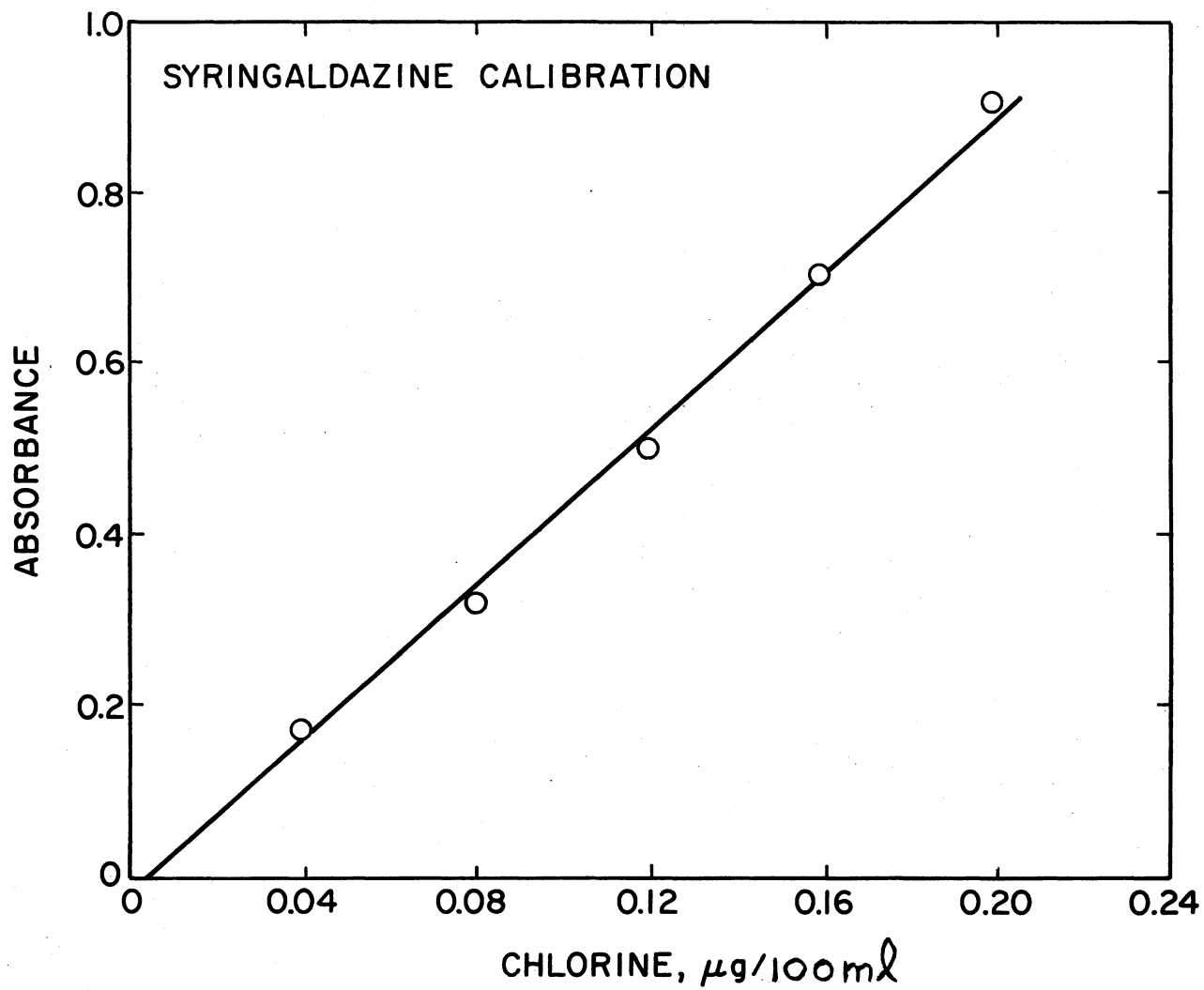
Figure 6. Syringaldazine Calibration

If the concentration of syringaldazine is below $10^{-5}\underline{M}$ and the chlorine

concentration is one ppm or less the amount of color produced is chlorine

dependent. Although a slight deviation from Beer's law occurs at high

concentrations, this was not a problem with concentrations below one ppm.

Laboratory Experiments

Experimental Procedure

Samples of a heterogenous laboratory culture of algae were placed

in 800 ml of distilled water containing various amounts of chlorine and

chloramine. The samples were incubated for two hours in a glove box

maintaining a slight positive pressure with N_2 gas to exclude laboratory

fumes (29). At the end of the incubation period analysis of the residual

chlorine was made.

A "matrix" experiment was conducted with total free chlorine added

as one element and chloramine as the other element in this 4 x 4 matrix.

The chloramine solution was made by preparing a solution with equal

molar concentrations of chlorine and ammonia. This produces a near

complete reaction between the chlorine and ammonia to form chloramine.

From the total chlorine and ammonia levels added the equilibrium con-

centrations of all species were calculated. Figure 7 shows the make-up

of the matrix. Table II gives the equilibrium concentrations. Initial

chloride that might be present was measured by titration with $AgNO_3$

using Ag/S electrode. pH measurements were taken before and after the

incubation. Total residual chlorine, free chlorine residual, and mono-

chloramine were measured by an amperometric technique.

CHLORINE ADDED (mg/ℓ) NH₂Cl ADDED (mg/ℓ)	0.10	0.20	0.40	1.0
0.10	BOTTLE 11	BOTTLE 12	BOTTLE 13	BOTTLE 14
0.20	BOTTLE 21	BOTTLE 22	BOTTLE 23	BOTTLE 24
0.40	BOTTLE 31	BOTTLE 32	BOTTLE 33	BOTTLE 34
1.0	BOTTLE 41	BOTTLE 42	BOTTLE 43	BOTTLE 44

Figure 7.   Chlorine - Chloramine Matrix

TABLE II

INITIAL EQUILIBRIUM CONCENTRATIONS OF CHLORINE AND CHLORAMINE

EXPERIMENT OF 2/ 0/75

BOTTLE	TOTAL CL2	TOTAL NH3	PH	HOCL	OCL-	CL2	CL-	NH3	NH4+	NH2CL	NHCL2
11	2.400E-01	3.900E-02	8.200	2.703E-03	1.371E-02	2.930E-13	1.200E-01	1.239E-04	1.415E-03	8.612E-02	1.747E-02
12	3.200E-C1	3.900E-02	8.200	6.980E-03	3.540E-02	1.009E-12	1.600E-01	4.300E-05	4.911E-04	7.719E-02	4.043E-02
13	4.800E-01	3.900E-02	8.190	1.729E-02	8.570E-02	3.837E-12	2.400E-01	1.341E-05	1.567E-04	5.963E-02	7.738E-02
14	9.600E-01	3.900E-02	8.180	5.395E-02	2.613E-01	2.450E-11	4.800E-01	2.352E-06	2.812E-05	3.263E-02	1.321E-01
21	4.000E-01	7.900E-02	8.210	1.281E-03	6.645E-03	2.261E-13	2.000E-01	5.322E-04	5.940E-03	1.752E-01	1.684E-02
22	4.800E-01	7.900E-02	8.210	3.618E-03	1.878E-02	7.667E-13	2.400E-01	1.840E-04	2.053E-03	1.711E-01	4.646E-02
23	6.400E-01	7.900E-02	8.200	1.068E-02	5.415E-02	3.087E-12	3.200E-01	5.159E-05	5.892E-04	1.417E-01	1.135E-01
24	1.120E 00	7.900E-02	8.170	4.159E-02	1.968E-01	2.255E-11	5.600E-01	7.297E-06	8.929E-05	7.803E-02	2.435E-01
31	7.100E-01	1.580E-01	8.210	6.890F-04	3.576E-03	2.160E-13	3.550E-01	1.882E-03	2.101E-02	3.335E-01	1.724E-02
32	8.000E-01	1.580E-01	8.210	1.472E-03	7.640E-03	5.199E-13	4.000E-01	9.299E-04	1.038E-02	3.520E-01	3.888E-02
33	9.600E-01	1.580E-01	8.200	4.772E-03	2.420E-02	2.069E-12	4.800E-01	2.707E-04	3.091E-03	3.321E-01	1.189E-01
34	1.440E 00	1.580E-01	8.180	2.319E-02	1.123E-01	1.580E-11	7.200E-01	3.577E-05	4.278E-04	2.133E-01	3.712E-01
41	1.680E 00	3.950E-01	8.200	5.461E-04	2.770E-03	4.145E-13	8.400E-01	5.724E-03	6.537E-02	8.037E-01	3.294E-02
42	1.760E 00	3.950E-01	8.190	7.089F-04	3.513E-03	5.768E-13	8.800E-01	4.562E-03	5.331E-02	8.315E-01	4.423E-02
43	1.920E 00	3.950E-01	8.190	1.237E-03	6.131E-03	1.098E-12	9.600E-01	2.740E-03	3.202E-02	8.717E-01	8.092E-02
44	2.400E 00	3.950E-01	8.160	6.097E-03	2.820E-02	7.249E-12	1.200E 00	5.101E-04	6.388E-03	7.997E-01	3.659E-01

CL CONTAINING SPECIES IN PPM AS CL, NON-CL CONTAINING SPECIES IN PPM AS N

Chloride Analysis

Determination was made of initial chloride in the water in which the algae and chlorine were added. Titration of the sample was made using $2.82 \times 10^{-3} \underline{M}$ AgNO$_3$. Excess Ag$^+$ was measured with a Ag/S electrode (Orion, 94-16-00), a reference electrode (Orion, 90-01-00), and a digital pH meter (Orion, 801) (30). The reference electrode was separated from the sample solution with a saturated KI salt bridge made of tygon tubing plugged with unfired Vircor (Corning, 7930). One hundred ml of sample was placed in a constant temperature water bath beaker with two drops of 1 $\underline{M}$ KNO$_3$ to give a constant ionic strength background. The AgNO$_3$ titrant was added and the millivolt reading noted after each addition. The millivolt readings were plotted on Gran's Plot Paper (Orion, 90-00-90) with millivolt response on the vertical axis and volume of titrant on the horizontal axis. A straight line is drawn through the last four points and the concentration of chloride in ppm is read as the intercept on the horizontal axis. Table III gives chloride values for the distilled water used in this experiment. A typical Gran's plot is shown in Figure 7.

Residual Chlorine Analysis

Apparatus. The amperometric method was used to determine the total residual chlorine and monochloramine levels (16). A platinum screen electrode, an Orion reference electrode filled with NaCl solution saturated with Ag$^+$, and a digital volt meter (Fairchild, 7050) with a 52 Kohm shunt comprise the end-point detection apparatus. (The reference electrode was separated from the sample beaker with the salt bridge described above.)

TABLE III

CHLORIDE DETERMINATIONS

Sample	Chloride (ppm)
1	0.003
2	-0.002
3	0.000
4	0.004
5	0.002
6	-0.003

The standard phenylarsine oxide titrant was standardized by amero-metric titration with standard iodine solution. The iodine solution was standardized against a 0.1 $\underline{N}$ sodium arsenite solution using starch as an indicator. (See Appendix C for standardization data.)

One modification of the referenced method was made. Nitrogen gas was bubbled through the sample solution to prevent reaction of the chlorine with the air. Without the use of the nitrogen severe drift occurred in the DVM reading. Table IV gives a comparison of a titration of a 1.0 ppm chlorine solution using the nitrogen and a titration without the nitrogen.

Total Residual Chlorine. One ml of acetate buffer (pH 4) and one ml of 0.3 $\underline{N}$ KI solution were added to the sample solution. The titrant is added until no additional response is noted on the DVM. The last increment which produced no change in response was subtracted to obtain the end point. Duplicate titrations were performed on samples from each bottle in the matrix. Table V gives the titration data for the total residual chlorine determinations.
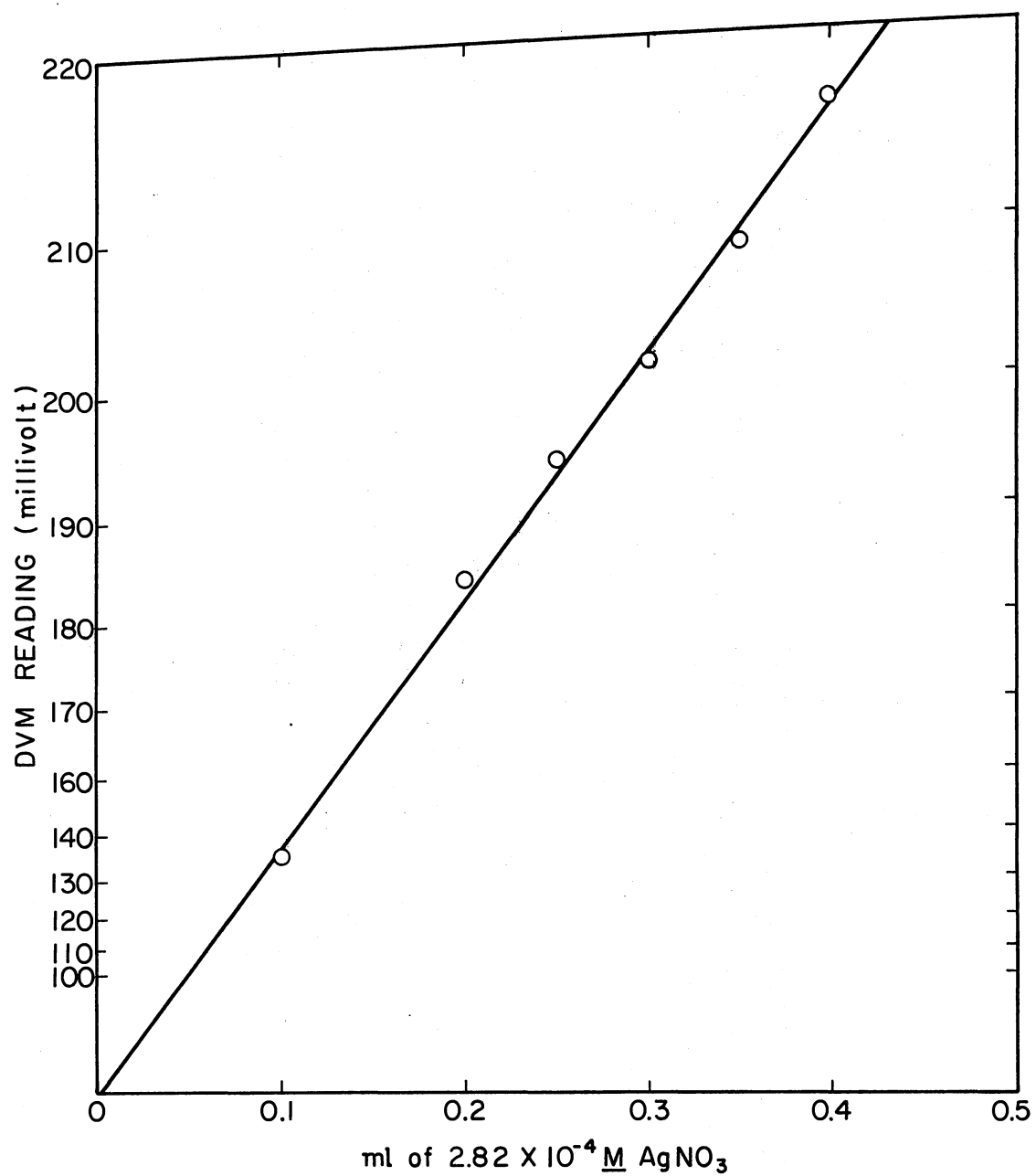
Figure 8. Titration of Chloride

TABLE IV

AMPEROMETRIC TITRATION OF 1.0 PPM TOTAL CHLORINE

ml of 5.64 N Phenylarsine Oxide Added	DVM Reading (Millivolts)	
	With N_2	Without N_2
0	0.90	0.90
1.00	0.84	0.85
2.00	0.81	0.82
3.00	0.79	0.79
4.00	0.77	0.76
4.25	0.65	0.33*
4.50	0.51	0.33
4.60	0.37	0.32
4.65	0.35	0.32
4.70	0.34	0.32
4.72	0.33	----**
4.75	0.32	0.32
4.80	0.32	0.31
5.00	0.32	0.31

*Severe downward drift of DVM read out

**Reading not taken

TABLE V

TOTAL RESIDUAL CHLORINE TITRATION DATA

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 11	
0	0.91	0.89
0.40	0.85	0.82
0.50	0.54	0.52
0.51	0.33	0.34
0.52	0.33	0.33
0.53	0.33	0.33
	Bottle 12	
0	0.93	0.91
0.50	0.91	0.90
1.00	0.82	0.79
1.10	0.68	0.65
1.12	0.39	0.38
1.13	0.32	0.33
1.14	0.32	0.32
1.15	0.32	0.32
	Bottle 13	
0	0.89	0.90
0.50	0.62	0.66
0.56	0.43	0.45
0.57	0.38	0.40
0.58	0.33	0.35
0.59	0.33	0.32
0.60	0.33	0.32
	Bottle 14	
0	0.97	0.95
1.0	0.93	0.90
2.0	0.87	0.83
2.5	0.69	0.65
2.6	0.48	0.44
2.3	0.37	0.33
2.4	0.32	0.33
2.5	0.32	0.33

TABLE V (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 21	
0	0.92	0.91
1.00	0.86	0.87
1.40	0.71	0.72
1.45	0.59	0.61
1.47	0.46	0.48
1.48	0.34	0.36
1.49	0.34	0.33
1.50	0.34	0.33
	Bottle 22	
0	0.92	0.91
1.00	0.81	0.79
1.75	0.70	0.68
1.90	0.52	0.50
1.93	0.32	0.38
1.94	0.32	0.35
1.95	0.32	0.32
1.96	0.32	0.32
	Bottle 23	
0	0.89	0.90
0.50	0.72	0.68
0.60	0.50	0.47
0.61	0.38	0.34
0.62	0.34	0.34
0.63	0.34	0.34
	Bottle 24	
0	0.92	0.89
1.50	0.77	0.71
1.70	0.64	0.58
1.71	0.52	0.34
1.72	0.35	0.34
1.73	0.32	0.34
1.74	0.32	0.34

TABLE V (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 31	
0	0.97	0.95
2.00	0.81	0.78
2.40	0.58	0.60
2.45	0.49	0.34
2.46	0.42	0.34
2.47	0.35	0.34
2.48	0.35	0.34
	Bottle 32	
0	0.92	0.89
3.50	0.83	0.78
3.60	0.72	0.36
3.61	0.58	0.36
3.62	0.35	0.36
3.63	0.35	0.36
	Bottle 33	
0	0.97	0.95
3.50	0.68	0.75
3.90	0.54	0.58
3.92	0.43	0.46
3.93	0.34	0.38
3.94	0.34	0.33
3.95	0.34	0.33
	Bottle 34	
0	0.89	0.90
1.00	0.73	0.71
1.30	0.54	0.50
1.35	0.45	0.33
1.36	0.37	0.33
1.37	0.32	0.33
1.38	0.32	0.33
	Bottle 41	
0	0.99	1.02
4.50	0.78	0.74
4.80	0.65	0.59
4.86	0.58	0.48
4.88	0.40	0.33
4.89	0.32	0.33
5.00	0.32	0.33

TABLE V (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 42	
0	1.06	1.04
6.00	0.77	0.81
6.10	0.70	0.72
6.12	0.58	0.56
6.14	0.43	0.36
6.15	0.35	0.36
6.16	0.32	0.36
6.17	0.32	0.36
	Bottle 43	
0	1.12	1.10
7.00	0.85	0.81
7.40	0.62	0.58
7.42	0.54	0.55
7.44	0.34	0.44
7.45	0.34	0.38
7.46	0.34	0.32
7.47	0.34	0.32
	Bottle 44	
0	1.22	1.19
8.00	0.77	0.83
8.30	0.62	0.66
8.33	0.50	0.57
8.34	0.35	0.41
8.35	0.35	0.35
8.36	0.35	0.32
8.37	0.35	0.32

Titrant: 1.00 ml of $5.64 \times 10^{-3}\underline{N}$ phenylarsine oxide = 0.20 ppm chlorine

DVM reading: volts

Table VI gives the values obtained for the total residual chlorine.

TABLE VI

TOTAL RESIDUAL CHLORINE

Bottle	Total Chlorine (ppm)
11	0.123
12	0.224
13	0.117
14	0.527
21	0.297
22	0.368
23	0.123
24	0.344
31	0.592
32	0.722
33	0.787
34	0.272
41	0.977
42	1.230
43	1.490
44	1.670

Free Chlorine Residual. One ml of pH 7 phosphate buffer was added to another sample. The sample was then titrated as above. The titration data for the residual free chlorine determinations are given in Table VII. Table VIII gives the residual free chlorine concentrations obtained. A dash (-) indicates that the first drop of titrant reacted all of the free chlorine present and therefore no determination was possible for these samples. Figure 9 gives a plot of the data for Bottle 33 to illustrate the shape of an amperometric titration.

TABLE VII

TITRATION DATA FOR RESIDUAL FREE CHLORINE

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 11	
0	0.39	0.38
0.01	0.34	0.34
0.02	0.34	0.34
1.00	0.34	0.34
5.00	0.33	0.33
	Bottle 12	
0	0.50	0.52
0.10	0.44	0.47
0.13	0.33	0.37
0.14	0.33	0.32
0.15	0.33	0.32
	Bottle 13	
0	0.42	0.44
0.05	0.33	0.34
0.06	0.33	0.33
0.07	0.33	0.33
	Bottle 14	
0	0.88	0.91
0.60	0.49	0.54
0.68	0.35	0.37
0.69	0.35	0.33
0.70	0.35	0.33
	Bottle 21	
0	0.41	0.42
0.01	0.34	0.35
0.02	0.34	0.35
1.00	0.34	0.35
5.00	0.34	0.34
	Bottle 22	
0	0.49	0.51
0.05	0.34	0.38
0.06	0.34	0.33
0.07	0.34	0.33
0.08	0.34	0.33

TABLE VII (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 23	
0	0.34	0.33
0.01	0.34	0.33
0.02	0.34	0.33
1.00	0.34	0.33
5.00	0.33	0.33
	Bottle 24	
0	0.45	0.42
0.01	0.35	0.36
0.02	0.35	0.36
1.00	0.35	0.36
5.00	0.34	0.35
	Bottle 31	
0	0.57	0.56
0.05	0.38	0.39
0.07	0.34	0.37
0.08	0.34	0.33
0.09	0.34	0.33
	Bottle 32	
0	0.65	0.67
0.06	0.51	0.54
0.07	0.42	0.45
0.08	0.35	0.38
0.09	0.35	0.32
0.10	0.35	0.32
	Bottle 33	
0	0.93	0.92
0.05	0.90	0.88
0.10	0.82	0.82
0.15	0.58	0.57
0.20	0.42	0.41
0.25	0.34	0.35
0.30	0.32	0.32
0.40	0.32	0.32

TABLE VII (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 34	
0	0.36	0.35
0.01	0.33	0.34
0.02	0.33	0.34
1.00	0.33	0.34
5.00	0.33	0.33
	Bottle 41	
0	0.35	0.34
0.01	0.34	0.33
0.02	0.34	0.33
1.00	0.34	0.33
5.00	0.33	0.32
	Bottle 42	
0	0.36	0.34
0.01	0.34	0.33
0.02	0.34	0.33
1.00	0.34	0.33
5.00	0.33	0.33
	Bottle 43	
0	0.38	0.37
0.01	0.35	0.35
0.02	0.35	0.35
1.00	0.35	0.35
5.00	0.34	0.34
	Bottle 44	
0	0.34	0.33
0.01	0.34	0.32
0.02	0.34	0.32
1.00	0.34	0.32
5.00	0.33	0.32

Titrant: 5.64 x 10^{-3} $\underline{N}$ phenylarsine oxide

DVM reading: volts
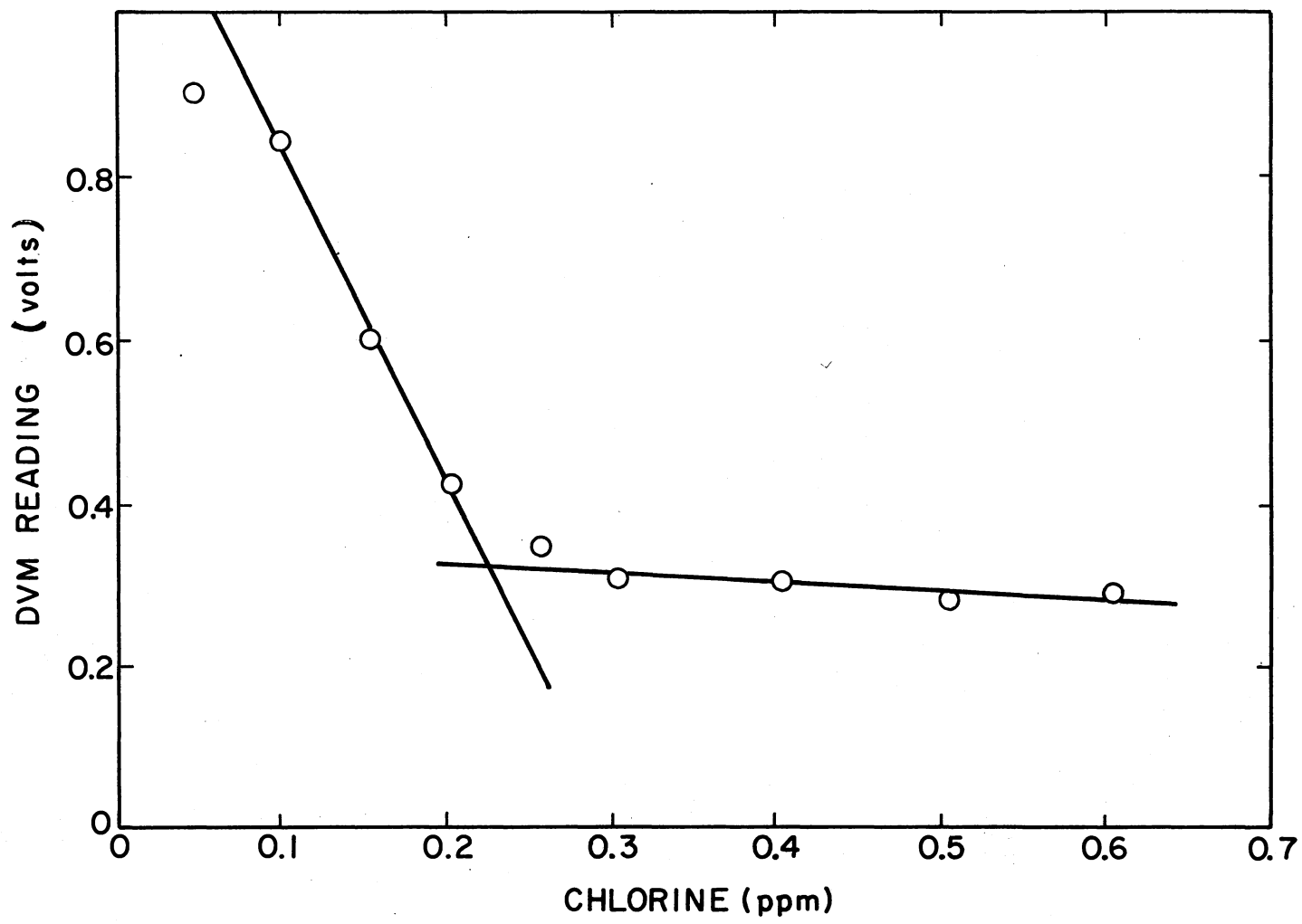
Figure 9. Amperometric Titration for Residual Free Chlorine

TABLE VIII

RESIDUAL FREE CHLORINE

Bottle	Free Chlorine (ppm as Cl)
11	---
12	0.027
13	0.010
14	0.138
21	---
22	0.012
23	---
24	---
31	0.015
32	0.017
33	0.045
34	---
41	---
42	---
43	---
45	---

Monochlorine Residual. After the titration for free chlorine, 0.2 ml KI solution was added to the sample. The titration was continued until another end-point was reached. The number of equivalents of phenylarsine oxide used in this titration was due to monochloramine. Titration data for the monochloramine residual are given in Table IX. The values for the residual monochloramine obtained from these titrations are given in Table X.

TABLE IX

TITRATION DATA FOR RESIDUAL MONOCHLORAMINE

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 11	
0	1.03	1.05
0.20	0.66	0.61
0.28	0.54	0.50
0.29	0.48	0.43
0.30	0.42	0.43
0.31	0.42	0.43
	Bottle 12	
0	1.10	1.12
0.20	0.72	0.70
0.30	0.58	0.54
0.33	0.44	0.45
0.34	0.44	0.43
0.35	0.44	0.43
0.36	0.44	0.43
	Bottle 13	
0	1.02	1.03
0.20	0.64	0.70
0.27	0.53	0.59
0.28	0.47	0.51
0.29	0.42	0.46
0.30	0.42	0.43
0.31	0.42	0.43
	Bottle 14	
0	0.99	0.97
0.10	0.68	0.71
0.20	0.51	0.55
0.21	0.42	0.46
0.22	0.42	0.43
0.23	0.42	0.43

TABLE IX (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 21	
0	1.20	1.19
0.50	0.87	0.91
0.60	0.62	0.67
0.68	0.45	0.49
0.69	0.45	0.45
0.70	0.45	0.43
0.71	0.45	0.43
	Bottle 22	
0	1.21	1.19
0.70	0.92	0.85
0.75	0.69	0.63
0.76	0.50	0.43
0.77	0.45	0.43
0.78	0.42	0.43
0.79	0.42	0.43
	Bottle 23	
0	0.97	0.96
0.25	0.73	0.68
0.30	0.57	0.43
0.31	0.41	0.43
0.32	0.41	0.43
	Bottle 24	
0	1.09	1.06
0.50	0.80	0.77
0.70	0.71	0.65
0.75	0.56	0.52
0.76	0.44	0.43
0.77	0.44	0.43
	Bottle 31	
0	1.18	1.16
1.00	0.87	0.84
1.20	0.63	0.59
1.21	0.52	0.50
1.22	0.42	0.45
1.23	0.42	0.43
1.25	0.42	0.43

TABLE IX (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 32	
0	1.22	1.20
1.00	0.83	0.90
1.20	0.68	0.73
1.40	0.57	0.61
1.41	0.50	0.49
1.42	0.47	0.43
1.43	0.45	0.43
1.44	0.45	0.43
	Bottle 33	
0	1.21	1.23
1.00	0.88	0.89
1.30	0.71	0.69
1.37	0.59	0.56
1.38	0.51	0.50
1.39	0.45	0.46
1.40	0.45	0.43
1.41	0.45	0.43
	Bottle 34	
0	1.11	1.09
0.50	0.86	0.82
0.60	0.64	0.67
0.65	0.55	0.57
0.66	0.49	0.48
0.67	0.44	0.43
0.68	0.44	0.43
0.69	0.44	0.43
	Bottle 41	
0	1.25	1.23
2.00	0.88	0.81
2.40	0.55	0.61
2.41	0.44	0.48
2.42	0.44	0.43
2.43	0.44	0.43

TABLE IX (CONTINUED)

ml Titrant	Trial 1 Voltage	Trial 2 Voltage
	Bottle 42	
0	1.27	1.26
2.00	0.92	0.90
3.00	0.52	0.53
3.01	0.45	0.46
3.02	0.45	0.43
3.03	0.45	0.43
	Bottle 43	
0	1.28	1.27
2.00	0.96	0.93
3.00	0.73	0.70
3.60	0.51	0.46
3.61	0.44	0.46
3.62	0.44	0.46
	Bottle 44	
0	1.31	1.27
3.00	0.99	0.97
4.00	0.83	0.85
4.10	0.75	0.71
4.13	0.53	0.52
4.14	0.46	0.45
4.15	0.44	0.45
4.16	0.44	0.45

Titrant: 5.64×10^{-3} $\underline{N}$ phenylarsine oxide

DVM reading: volts

TABLE X

RESIDUAL MONOCHLORAMINE

Bottle	Monochloramine (ppm)
11	0.058
12	0.068
13	0.058
14	0.042
21	0.138
22	0.154
23	0.061
24	0.152
31	0.245
32	0.285
33	0.278
34	0.134
41	0.482
42	0.603
43	0.721
44	0.829

CHAPTER IV

EXPERIMENTAL RESULTS

Nitrate Uptake by Algae as a Function of

Chlorine and Chloramine Concentration

To investigate the uptake rate of nitrate by freshwater phylo-
plankton as a function of chlorine and chloramine, a constant amount of
$^{15}N\text{-}NO_3^-$ and varying amounts of chlorine and chloramine were added to
the lake water samples. After the incubation period, the samples were
combusted and ^{15}N atom percent determinations made by mass spectrometry.
From these ^{15}N percent values the nitrate uptake rate, $V_{NO_3^-}$, was cal-
culated (31) (Appendix B). The equilibrium concentrations of free and
bound chlorine in the samples were calculated by the computer program
discussed in Chapter II. The levels of chlorine and chloramine added,
equilibrium levels of free and bound chlorine, and $V_{NO_3^-}$ values are given
in Table XI.

Results

The Statistical Analysis System was used to determine coefficients
for terms of an equation to describe the surface formed in terms of
$V_{NO_3^-}$ vs free chlorine, (X), and chloramine, (Y), concentrations (32).
The resulting surface is shown in Figure 10. There appears to be a
decreasing parabolic response of $V_{NO_3^-}$ along the free chlorine axis.

TABLE XI

THE EFFECT OF CHLORINE AND CHLORAMINE ON $V_{NO_3^-}$

Element Number	Cl_2 Added (ppm)	Chloramine Added (ppm)	Equilibrium Free Cl_2 (ppm) (Cl_2,HOCl,OCl$^-$)	Equilibrium Bond Cl_2 (ppm) (NH_2Cl,$NHCl_2$)	$V_{NO_3^-}$ x 10^3 (hr^{-1})	
					Bottle 1	Bottle 2
1,1	0.00	0.00	0.00	0.00	3.976	1.503
1,2	0.00	0.025	8.46×10^{-4}	1.17×10^{-2}	2.276	2.197
1,3	0.00	0.050	5.46×10^{-3}	1.95×10^{-2}	2.740	0.577
1,4	0.00	0.125	3.88×10^{-2}	2.37×10^{-2}	1.640	1.689
2,1	0.025	0.00	7.89×10^{-4}	2.42×10^{-2}	1.140	1.146
2,2	0.025	0.025	2.20×10^{-3}	3.53×10^{-2}	1.274	0.894
2,3	0.025	0.050	6.82×10^{-3}	4.32×10^{-2}	1.344	1.682
2,4	0.025	0.125	3.69×10^{-2}	5.06×10^{-2}	2.141	2.178
3,1	0.050	0.00	1.53×10^{-3}	4.85×10^{-2}	0.551	0.557
3,2	0.050	0.025	3.29×10^{-3}	5.93×10^{-2}	0.430	0.435
3,3	0.050	0.050	7.82×10^{-3}	6.72×10^{-2}	0.449	*
3,4	0.050	0.125	3.51×10^{-2}	7.74×10^{-2}	0.506	0.620
4,1	0.125	0.00	3.32×10^{-3}	1.22×10^{-1}	0.227	0.317
4,2	0.125	0.025	5.50×10^{-3}	1.32×10^{-1}	0.249	0.633
4,3	0.125	0.050	9.44×10^{-3}	1.41×10^{-1}	0.172	0.168
4,4	0.125	0.125	3.08×10^{-2}	1.57×10^{-1}	0.084	0.127

*sample lost
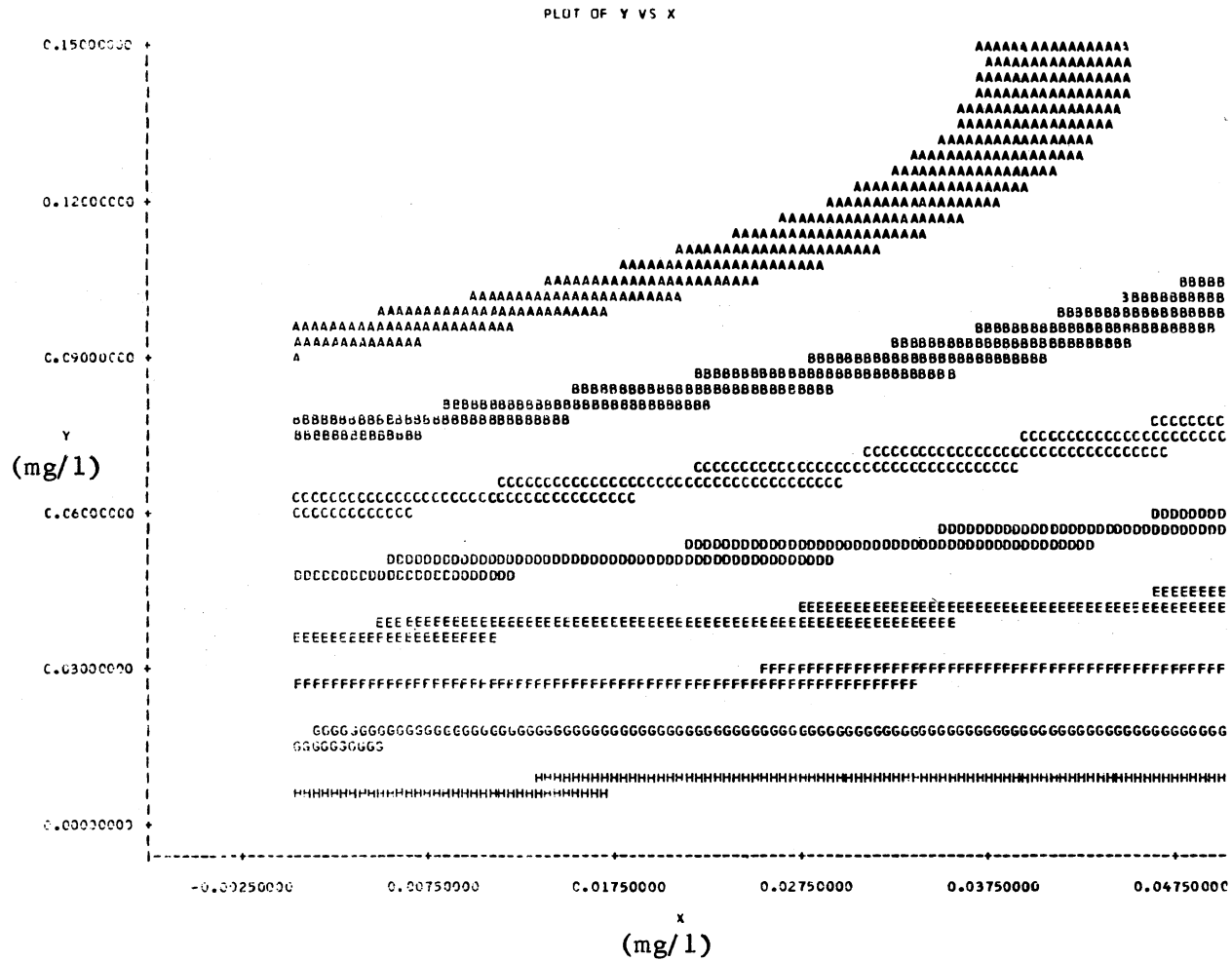
Figure 10. Plot of $V_{NO_3^-}$ vs. Free Chlorine vs. Chloramine

45

Discussion

The relative small change in response along the chlorine axis may be due to the "break point" reaction. As the ratio of total initial chlorine to total initial ammonia increases a sudden loss of residual chlorine occurs. This phenomenon was reported by Griffin in 1939. This reaction occurs most rapidly at a pH near 8 (13). The lake water before and after the addition of reagents was found to have a pH of 8.5. The relative minimum of residual chlorine occurs at a weight ratio of chlorine to ammonia-nitrogen of 10:1, Figure 2. The reaction requires one-half hour for ammonia-nitrogen concentrations below one ppm (6).

The ambient ammonia-nitrogen level for this experiment was 0.0086 ppm. The largest spike of chlorine was 0.10 ppm. The "break point" minima was exceeded in only one set of duplicates with a ratio of 11.6:1. Therefore, no bottles in this experiment had a great excess of chlorine corresponding to the linear portion of the residual chlorine curve given in Figure 2.

It would be expected that the $V_{NO_3^-}$ vs chlorine plot for constant ammonia nitrogen should be the inverse of the residual chlorine plot. When residual chlorine is high, $V_{NO_3^-}$ should be low. This response was hard to detect over the narrow chlorine concentrations used due to a relatively high error in some of the duplicates of the various chlorine concentrations used.

In order to determine if the "break point" reaction is responsible for the small response along the chlorine axis, additional experiments would be necessary using chlorine concentrations in excess of the 10:1 chlorine to ammonia-nitrogen ratio. A surface such as that given in Figure 11 would be the expected result from such work.
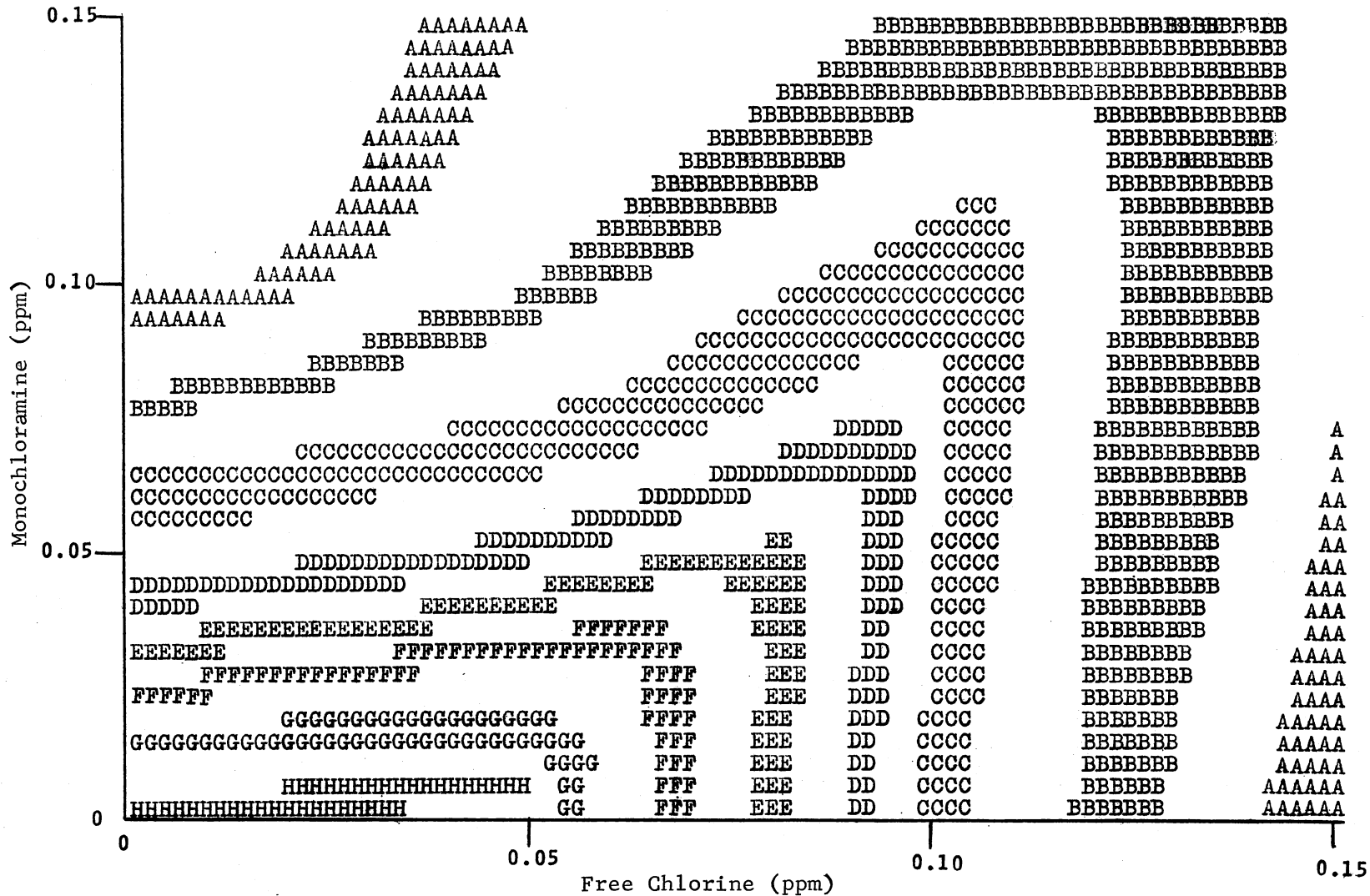
Figure 11. Plot of the Predicted Surface for $V_{NO_3^-}$ vs. Free Chlorine vs. Chloramine

Residual Chlorine After the Incubation Period

After the incubation period 50 ml aliquots of lake water were removed from the sample bottles before the Lugol's solution was added. These 50 ml samples were analyzed for free chlorine, Cl_2, HOCl, and OCl^-, by the syringaldazine method described in Chapter III. pH measurements were also taken.

In order to calculate all of the chemical species involved in the chlorine-chloramine equilibrium system three species must be measured. However, time and manpower were not sufficient to run ammonia analysis on all of the sample bottles. Since the ^{15}N spikes were set at 20 percent of the ambient level, it seems reasonable that no more than approximately 20 percent of the ammonia would be removed from the lake water during the incubation period by the algae. This would bring the ammonia concentration back to approximately the level of the lake water before the spike.

Results

Computer calculations were made with 20, 10, 5, 3, and 1 percent of the total ammonia concentration removed. This caused a variation in the calculated values for total residual chlorine less than five percent. A set of calculated values are given in Table XII. Data for total residual chlorine calculated in the manner described above are plotted against initial total chlorine in Figure 12.

Discussion

Since the data are from experiments conducted on two different days during the summer of 1974 and the ammonia levels were not the same

TABLE XII

CALCULATED RESIDUAL CONCENTRATIONS OF CHLORINE AND CHLORAMINE

AEC PROJECT: LCB
CL CONTAINING SPECIES IN PPM AS CL, NON-CL CONTAINING SPECIES IN PPM AS N

NH3 ABS	BOTTLE	TOTAL CL	TOTAL NH3	PH	HOCL	OCL-	CL2	CL-	NH3	NH4+	NH2CL	NHCL2
0.20	1	1.938E-02	1.615E-02	8.590	1.672E-05	2.082E-04	5.960E-17	9.684E-03	2.197E-03	1.022E-02	9.447E-03	1.185E-05
0.10	1	1.944E-02	1.817E-02	8.590	1.450E-05	1.805E-04	5.185E-17	9.714E-03	2.550E-03	1.186E-02	9.509E-03	1.035E-05
0.05	1	1.946E-02	1.918E-02	8.590	1.360E-05	1.693E-04	4.867E-17	9.726E-03	2.727E-03	1.269E-02	9.533E-03	9.726E-06
0.03	1	1.947E-02	1.958E-02	8.590	1.326E-05	1.651E-04	4.751E-17	9.731E-03	2.798E-03	1.302E-02	9.543E-03	9.498E-06
0.01	1	1.948E-02	1.999E-02	8.590	1.295E-05	1.612E-04	4.640E-17	9.735E-03	2.869E-03	1.335E-02	9.551E-03	9.280E-06
0.20	2	4.410E-02	1.615E-02	8.590	5.951E-05	7,409E-04	4.820E-16	2.200E-02	1.379E-03	6.417E-03	2.111E-02	9.427E-05
0.10	2	4.438E-02	1.817E-02	8.590	4.856E-05	6.045E-04	3.959E-16	2.215E-02	1.715E-03	7.981E-03	2.142E-02	7.805E-05
0.05	2	4.449E-02	1.918E-02	8.590	4.441E-05	5.529E-04	3.630E-16	2.221E-02	1.886E-03	8.774E-03	2.154E-02	7.178E-05
0.03	2	4.452E-02	1.958E-02	8.590	4.293E-05	5.345E-04	3.513E-16	2.223E-02	1.955E-03	9.093E-03	2.158E-02	6.953E-05
0.01	2	4.456E-02	1.999E-02	8.590	4.155E-05	5.173E-04	3.403E-16	2.225E-02	2.023E-03	9.413E-03	2.162E-02	6.741E-05
0.20	3	6.324E-02	1.615E-02	8.600	1.390E-04	1.771E-03	1.573E-15	3.147E-02	8.185E-04	3.721E-03	2.925E-02	3.051E-04
0.10	3	6.409E-02	1.817E-02	8.600	1.055E-04	1.344E-03	1.211E-15	3.193E-02	1.115E-03	5.068E-03	3.024E-02	2.394E-04
0.05	3	6.440E-02	1.918E-02	8.600	9.350E-05	1.191E-03	1.079E-15	3.209E-02	1.272E-03	5.785E-03	3.059E-02	2.146E-04
0.03	3	6.450E-02	1.958E-02	8.600	8.936E-05	1.138E-03	1.033E-15	3.215E-02	1.337E-03	6.077E-03	3.071E-02	2.059E-04
0.01	3	6.460E-02	1.999E-02	8.600	8.552E-05	1.090E-03	9.906E-16	3.220E-02	1.402E-03	6.373E-03	3.083E-02	1.978E-04
0.20	4	6.875E-02	1.615E-02	8.570	1.914E-04	2.275E-03	2.519E-15	3.415E-02	6.348E-04	3.093E-03	3.125E-02	4.485E-04
0.10	4	6.991E-02	1.817E-02	8.570	1.424E-04	1.693E-03	1.909E-15	3.478E-02	8.904E-04	4.338E-03	3.260E-02	3.483E-04
0.05	4	7.033E-02	1.918E-02	8.570	1.249E-04	1.484E-03	1.685E-15	3.501E-02	1.031E-03	5.021E-03	3.309E-02	3.100E-04
0.03	4	7.047E-02	1.958E-02	8.570	1.188E-04	1.413E-03	1.607E-15	3.509E-02	1.088E-03	5.303E-03	3.326E-02	2.965E-04
0.01	4	7.060E-02	1.999E-02	8.570	1.133E-04	1.347E-03	1.535E-15	3.516E-02	1.147E-03	5.589E-03	3.341E-02	2.840E-04
0.20	5	8.019E-02	1.615E-02	8.560	3.401E-04	3.952E-03	5.319E-15	3.966E-02	3.943E-03	1.966E-03	3.448E-02	8.800E-04
0.10	5	8.228E-02	1.817E-02	8.560	2.498E-04	2.903E-03	4.020E-15	4.078E-02	5.751E-03	2.867E-03	3.695E-02	6.927E-04
0.05	5	8.307E-02	1.918E-02	8.560	2.155E-04	2.504E-03	3.504E-15	4.123E-02	6.839E-03	3.410E-03	3.790E-02	6.127E-04
0.03	5	8.334E-02	1.958E-02	8.560	2.035E-04	2.364E-03	3.321E-15	4.138E-02	7.305E-03	3.642E-03	3.823E-02	5.837E-04
0.01	5	8.359E-02	1.999E-02	8.560	1.924E-04	2.236E-03	3.151E-15	4.152E-02	7.787E-03	3.882E-03	3.853E-02	5.564E-04
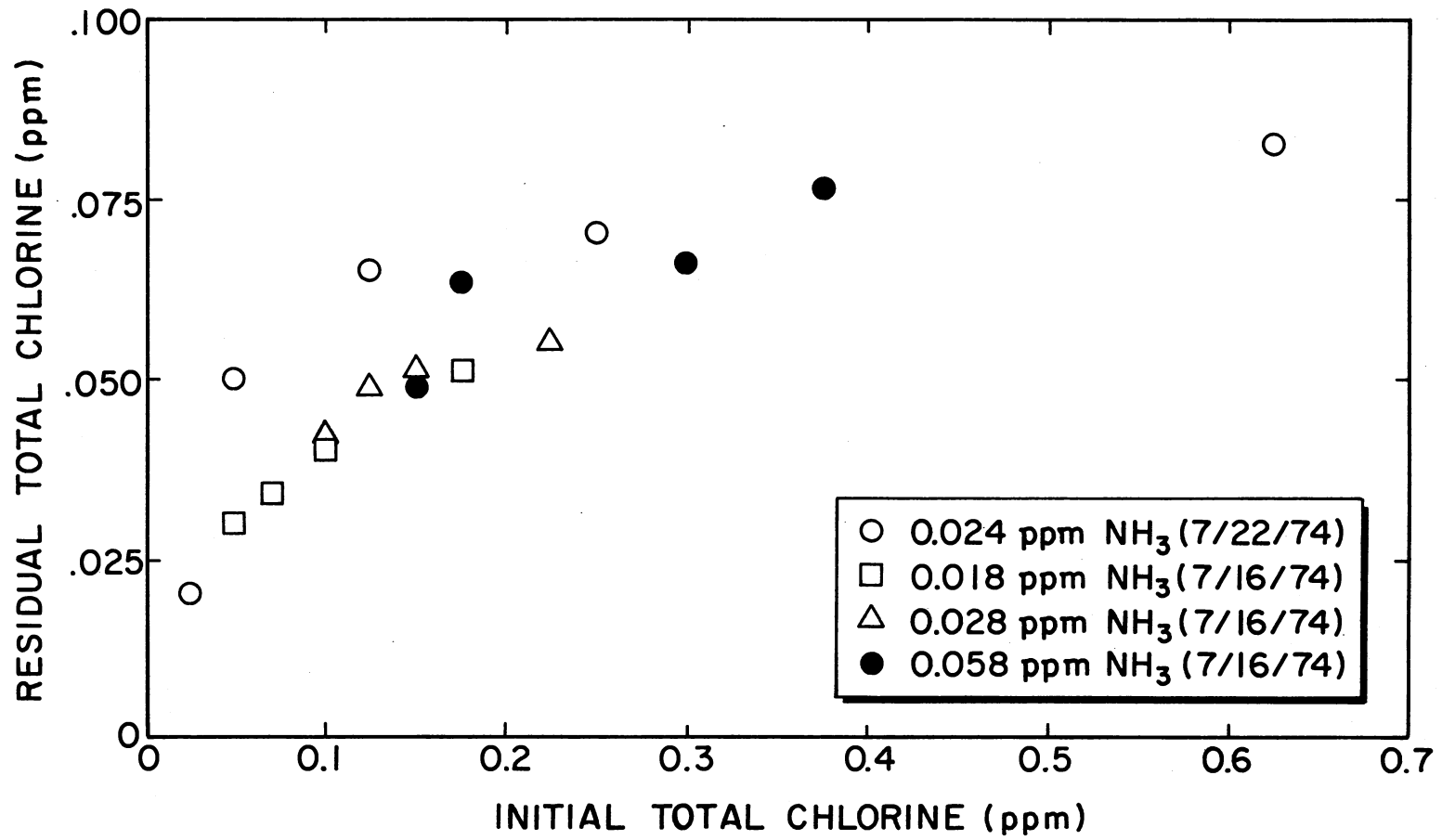
Figure 12. Residual Total Chlorine vs. Initial Total Chlorine

for all samples the points do not form a smooth curve. However, when a polynomial least squares fit is made of the data, an equation is obtained which will give an approximation of the total residual chlorine that can be expected after a 24-hour incubation period under varying conditions in Lake Carl Blackwell. The resulting equation is given below.

$$Y = 0.0244 + 0.1939X + (-0.1619X^2)$$

where Y = total residual chlorine and x = total initial chlorine. Table XIII gives the percent difference of the observed and calculated values. The least square fit was performed by a computer program in the public library of the Oklahoma State Computer Center. A plot of the equation is given in Figure 13.

Laboratory Experiments

Results

Chloride Determination. Distilled water was used in this experiment and determinations gave chloride levels that fluctuated slightly about zero. Table II gives chloride values for six determinations. Because of the extremely low level of chloride present, chloride was taken as zero in the equilibrium determinations. As described in Chapter III, the millivolt response was plotted against volume of titrant on Gran's Plot Paper, an antilog volume corrected graph paper.

Residual Chlorine-Chloramine Equilibrium System. Three analyses must be made in order to solve the system of equilibria equations. In this experiment four (pH, total available chlorine, free chlorine, and

TABLE XIII

FIT OF EQUATION FOR RESIDUAL TOTAL CHLORINE

X	Y	Y-CALC	DIFF	PCT-DIFF
.025000	.019460	.029163	-.009703	-33.271
.050000	.031750	.033708	-.001958	-5.808
.050000	.037190	.033708	.003482	10.331
.075000	.037190	.038050	-.000860	-2.260
.10000	.041020	.042100	-.001170	-2.773
.100000	.043200	.042100	.001010	2.394
.125000	.048270	.046127	.002143	4.645
.125000	.064400	.046127	.018273	39.613
.150000	.051690	.049863	.001827	3.665
.175000	.052000	.053395	-.001395	-2.613
.225000	.055120	.059853	-.004733	-7.908
.250000	.048460	.062779	-.014319	-22.809
.25000	.070330	.062779	.007551	12.028
.275000	.063830	.065502	-.001672	-2.553
.300000	.066210	.068023	-.001813	-2.665
.37500	.077010	.074370	.002640	3.549
.625000	.083070	.082373	.000697	.846

Standard Error of Estimate for Y = .007343559146232
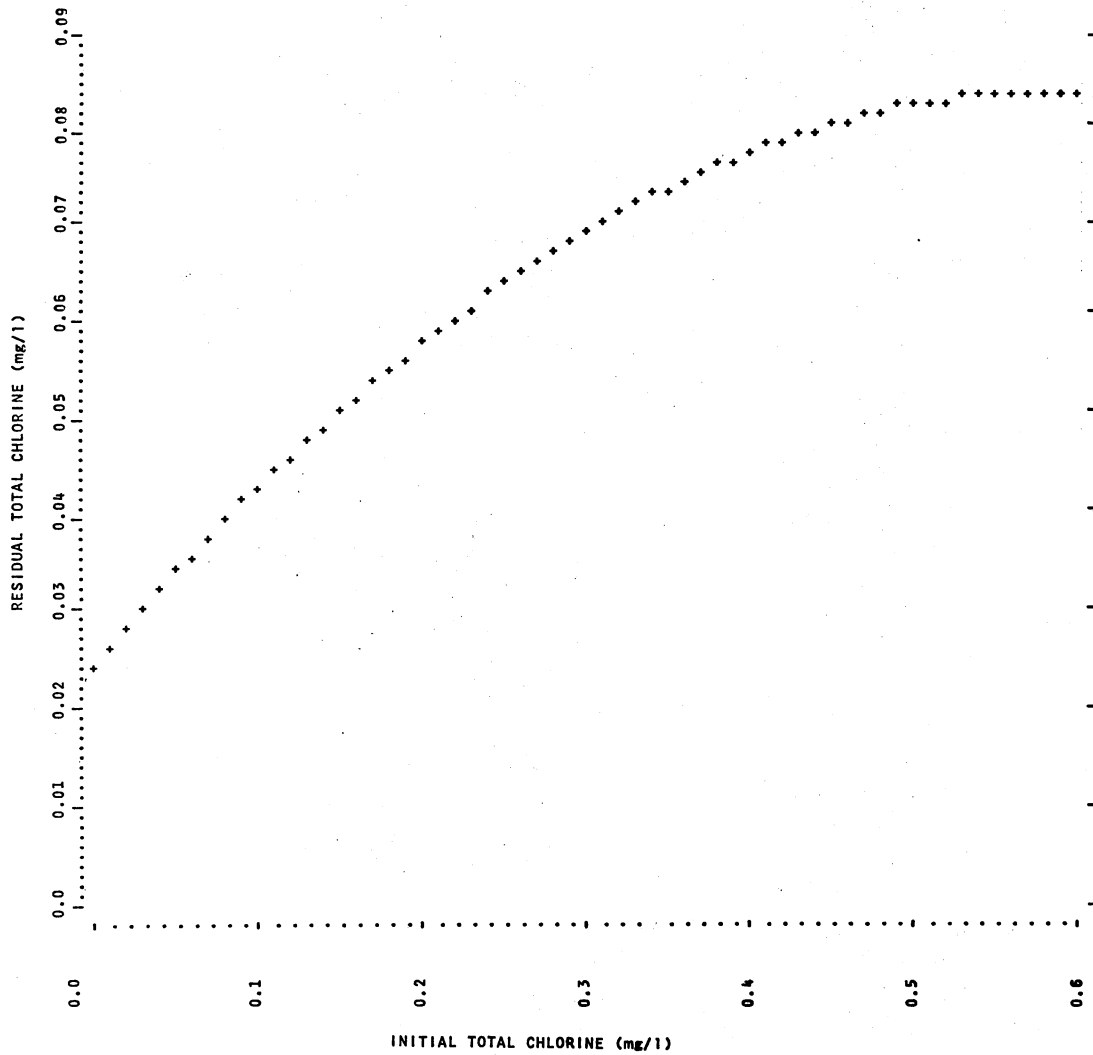
Figure 13. Calculated Residual Chlorine vs. Initial Total Chlorine

NH_2Cl) were made. Total available chlorine, pH, and NH_2Cl were used to solve the equilibria system. Free chlorine was used as a check against the calculated values. Table XIV gives the measured values of total chlorine, NH_2Cl, measured free chlorine and calculated free chlorine.

Discussion

For samples which had a measurable level of free chlorine the measured and calculated values agree within approximately 20% except for one case. This is not unexpected considering the complexity of the system, and low concentrations of the species present.

Summary

A computer program was developed which has the capacity to calculate the free chlorine, chloramine, and ammonia species present in a natural water system. A laboratory check of the calculated equilibrium calculations gave agreement within 20% for these samples.

The surface produced by plotting $V_{NO_3^-}$ vs. free chlorine vs. bound chlorine can be described by

$$V_{NO_3^-} = 2.45(10^{-4}) - 3.61(10^{-3})y + 1.13(10^{-2})y^2 + 8.56(10^{-3})xy$$

where y = bound chlorine concentration in ppm as Cl and x = free chlorine concentration in ppm as Cl for the concentration range studied. The relative small response along the free chlorine axis may have been due to reduction of chlorine to chloride ion by the "breakpoint" reaction.

Residual chlorine after the incubation period may be described by

$$y = 0.0244 + 0.1939x + (-0.1619x^2)$$

TABLE XIV

COMPARISON OF MEASURED AND CALCULATED RESIDUAL FREE CHLORINE

Bottle	pH	Total Chlorine (ppm as Cl)	NH_2Cl (ppm as Cl)	Measured Free Cl_2 (ppm as Cl)	Calculated Free Cl_2 (ppm as Cl)	% Difference $\frac{m-c}{m}$ x 100
11	8.17	1.23E-1	5.81E-2	*	1.95E-3	---
12	8.18	2.24E-1	6.78E-2	2.75E-2	2.36E-2	15.2
13	8.16	1.17E-1	5.59E-2	1.00E-2	1.51E-2	40.8
14	8.18	5.27E-1	4.24E-2	1.38E-1	1.43E-1	3.6
21	8.19	2.97E-1	1.38E-1	*	3.67E-3	---
22	8.16	E.68E-1	1.54E-1	1.25E-2	1.02E-2	20.2
23	8.20	1.23E-1	6.07E-2	*	4.25E-4	---
24	8.18	3.44E-1	1.52E-1	*	6.97E-3	---
31	8.20	5.92E-1	2.45E-1	1.50E-2	1.27E-2	16.4
32	8.17	7.22E-1	2.83E-1	1.75E-2	1.65E-2	5.9
33	8.18	7.87E-1	2.78E-1	4.50E-2	4.51E-2	0.2
34	8.19	2.72E-1	1.34E-1	*	1.03E-4	---
41	8.19	9.77E-1	4.82E-1	*	9.12E-4	---
42	8.19	1.23E 0	6.03 E-1	*	1.35E-3	---
43	8.17	1.49E 0	7.21E-1	*	2.31E-3	---
44	8.16	1.67E 0	8.29E-1	*	4.99E-4	---

*indicates concentration too low to measure

where y = residual chlorine in ppm as Cl and x is initial chlorine in

ppm as Cl. A wide range of ammonia concentrations was used and the

equation fit the observed residual within 25% for 15 of the 17 data

points.

A laboratory check of the calculated equilibrium calculations gave

agreement within 20% of calculated and observed free chlorine concentra-

tions for those samples containing enough free chlorine to be measured

by the amperometric method,

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APPENDIX A

COMPUTER PROGRAM FOR CHLORINE-CHLORAMINE

EQUILIBRIUM SYSTEM

```
          C                CHLORINE AND CHLORAMINE EQUILIBRIUM CALCULATIONS
          C
          C---->GENERAL PROGRAM WRITTEN BY A. J. BARD AND D. M. KING, UNIVERSITY OF
          C---->TEXAS, PUBLISHED IN J. OF CHEM. ED., 42, P. 127, 1965.
          C---->MODIFIED BY PAUL WHITFIELD AND L. P. VARGA, OKLAHOMA STATE UNIVERSITY,1974
          C
          C
          C---->VARIABLE DEFINATIONS:
          C---->CY(I) = CONC. OF NH2CL
          C---->MB(I) = BOTTLE NUMBER
          C---->C(J,I) = OUTPUT, J=BOTTLE COUNTER, I=CHEMICAL SPECIES COUNTER.
          C---->NB = TOTAL NUMBER OF BOTTLES IN EXPERIMENT.
          C---->MO = MONTH OF EXPERIMENT
          C---->NDAY = DAY   "        "
          C---->NYR = YEAR   "        "
          C---->SCLI = INITIAL CHLORIDE ION CONC. (PPM) IN THE LAKE WATER
          C---->CBNH3 = AMBIENT AMMONIA CONC. (PPM) IN THE LAKE WATER.
          C---->DIMENSION FOR CY(I) = 2
          C---->    "       "   MB(J) = NB
          C---->    "       "   C(J,I) = NB,11
0001            DIMENSION CY(2), MB(16), C(16,11)
0002            READ 98, MO, NDAY, NYR, SCLI, CBNH3, NB
          C---->PRINT TITLE FOR OUTPUT
0003            PRINT 99, MO, NDAY, NYR
0004            PRINT 102
0005            J = 1
0006            DO26 K=1,NB
          C---->KB = BOTTLE NUMBER
          C---->TCL = TOTAL CHLORINE CONC. IN PPM
          C---->TNH3 = TOTAL AMMONIA ADDED TO THE BOTTLE
          C---->PH = PH OF THE SOLUTION
0007            READ 101, KB, TCL, TNH3, PH
0008            TNH3 = TNH3 + CBNH3
          C---->CONVERSION OF PPM CONC. TO MOLAR CONC.
0009            TNH3 = TNH3/(14.0*1.0E 03)
0010            TCL = TCL/(35.45*1.0E 03)
0011            SCLI = SCLI/(35.45*1.0E 03)
0012            H = 10.0**(-PH)
          C---->INITIAL GUESS OF ONE SPECIES, INTENTIALLY SMALLER THAN TRUE VALUE:
          C---->CX = HOCL CONC.
00.3            CX = 1.0E-20
          C---->AK2 TO AKW ARE EQUILIBRIUM CONSTANTS.
0014            AK2 = 3.94E-04
0015            AK3 = 3.20E-08
0016            AK4 = 1.81E-05
0017            AK5 = 3.60E 09
0018            AK6 = 1.33E 06
0019            AKW = 1.00E-14
          C---->TEST LOOP TO SET 10**-ME LESS THAN TCL TO AVOID AN INFINITE LOOP LATER:
0020            ME = 1
0021        202 IF ((TCL/(10.0**(-ME))) - 1.0) 200,201,201
0022        200 ME = ME + 1
          C---->TEST FOR SIZE OF TCL, IF LESS THAN 10**-20, A WARNING STATEMENT IS PRINTED
          C---->AND PROGRAM TERMINATED
0023            IF (ME.GT.20) GO TO 300
0024            GO TO 202
0025        300 PRINT 301
0026            GO TO 303
```

```
                      C---->SET LX SO 10**-LX IS LESS THAN TCL.
0027                    201 LX = MF + 2
0028                        MX = 1
0029                     23 I = 1
0030                        ALX = LX
                      C---->TEST TO SEE IF INFINITE LOOP HAS DEVELOPED; IF SO, PROGRAM IS TERMINATED.
0031                        IF(LX.GT.TCL) GO TO 304
0032                        GO TO 15
0033                    304 PRINT 305
0034                        GO TO 303
                      C---->INITIAL GUESS OF SECOND SPECIES, ALSO INTENTIALLY SMALLER THAN TRUE VALUE:
                      C---->CY(I) = NH2CL CONC.
0035                     15 CY(I) = 1.0E-20
                      C---->INITIALIZE COUNTERS TO ONE:
0036                        JY = 1
0037                        LY = 1
0038                        MY = 1
0039                     11 ALY = LY
                      C---->CALCULATION OF REMAINING SPECIES:
                      C---->OH = HYDROXIDE ION CONC., ANH3 = AMMONIA CONC., ANH4 = AMMONIUM ION CONC.,
                      C---->ANCL2 = NHCL2 CONC., CLI = CHLORIDE ION CONC., AND CL2 = MOLECULAR
                      C---->CHLORINE CONC.
0040                        OH = AKW/H
0041                        OCL = AK3*CX/H
0042                        ANH3 = CY(I)/(AK5*CX)
0043                        ANH4 = AK4*ANH3/OH
0044                        ANCL2 = AK6*CX*CY(I)
0045                        CLI = CX + OCL + CY(I) + 2*ANCL2 + SCLI
0046                        CL2 = CX*H*CLI/AK2
0047                        JY = JY + 1
0048                        GO TO (1,2), I
                      C---->TEST EQUATION FOR CY(1):
0049                      1 Y = (2.0*CL2) + CX + OCL + CLI + CY(I) + (2.0*ANCL2) - (TCL+SCLI)
0050                        GO TO 7
                      C---->TEST EQUATION FOR CY(2):
0051                      2 Y = ANH3 + ANH4 + CY(I) + ANCL2 - TNH3
                      C---->IF 100 TRIALS HAVE NOT OBTAINED A SUITABLE CY(I), CHANGE CX AND CONTINUE.
0052                      7 IF(JY-100) 3,3,12
0053                      3 IF(MY-1) 4,4,5
0054                      4 Z1 = Y
0055                        MY = MY + 1
                      C---->"IF" STATEMENTS INCREASE OR DECREASE CY(I) DEPENDING UPON THE SIGN OF Y.
0056                      5 IF(Z1) 6,12,8
0057                      6 IF(Y) 9,12,10
0058                      8 IF(Y) 10,12,9
                      C---->INCREASING CY(I):
0059                      9 CY(I) = CY(I) + 10.0**(-ALY)
0060                        GO TO 11
                      C---->DECREASING CY(I):
0061                     10 CY(I) = CY(I) - 10.0**(-ALY)
0062                        LY = LY + 1
0063                        ALY = LY
                      C---->TERMINATION OF SEARCH FOR CY(I) AFTER FIFTH SIGNIFICANT DIGIT:
0064                        IF(CY(I)/10.0**(-ALY) - 10.0**5.0) 9,9,12
                      C---->IF I=1, BEGIN SEARCH FOR CY(2):
0065                     12 IF(I -1) 13,13,14
0066                     13 I = I + 1
0067                        GO TO 15
```

```
              C---->TEST TO SEE IF CY(1) = CY(2):
C068              14 Y = CY(2) - CY(1)
              C---->TEST TO SEE IF CY(1) = CY(2) WITHIN 10**-5 PERCENT:
0069                 IF(CY(1).GT.CY(2)) GO TO 25
C070                 IF(ABS(Y).LT.1.0E-07*CY(1)) Y = 0.0
C071                 GO TO 24
0072              25 IF(ABS(Y).LT.1.0E-07*CY(2)) Y = 0.0
0073              24 IF(MX - 1) 16,16,17
C074              16 Z2 = Y
              C---->"IF" STATEMENTS INCREASE OR DECREASE CX DEPENDING UPON THE SIGN OF Y.
0075                 MX = MX + 1
0076              17 IF(Z2) 18,19,20
CC77              18 IF(Y) 21,19,22
0078              20 IF(Y) 22,19,21
0079              21 CX = CX + 10.0**(-ALX)
CC8C                 GO TO 23
0081              22 CX = CX - 10.0**(-ALX)
0082                 LX = LX + 1
0083                 ALX = LX
              C---->TERMINATION OF SEARCH FOR CX AFTER FIFTH SIGNIFICANT DIGIT.
0084                 IF (CX/10.0**(-ALX) - (10.0**5.0)) 21,21,19
              C---->CONVERSION OF MOLAR CONCENTRATIONS TO PPM:
C085             19 TCL = TCL*35.45*1.0E 03
0086                 TNH3 = TNH3*14.0*1.0E 03
0087                 CX = CX*35.45*1.0E 03
0088                 OCL = OCL*35.45*1.0E 03
CC89                 CL2 = CL2*70.9*1.0E 03
0090                 CLI = CLI*35.45*1.0E 03
0091                 ANH3 = ANH3*14.0*1.0E 03
C092                 ANH4 = ANH4*14.0*1.0E 03
0093                 CY(I) = CY(I)*35.45*1.0E 03
0094                 ANCL2 = ANCL2*70.9*1.0E 03
              C---->STORAGE OF OUTPUT IN AN ARRAY FOR PRINTING OF A DUPLICATE COPY OF PUTPUT.
0095                 MB(J) = KB
C096                 C(J,1) = TCL
0097                 C(J,2) = TNH3
0098                 C(J,3) = PH
0099                 C(J,4) = CX
0100                 C(J,5) = OCL
0101                 C(J,6) = CL2
0102                 C(J,7) = CLI
0103                 C(J,8) = ANH3
0104                 C(J,9) = ANH4
0105                 C(J,10) = CY(I)
0106                 C(J,11) = ANCL2
              C---->PRINT OUTPUT:
C107                 PRINT 100,KB,TCL,TNH3,PH,CX,OCL,CL2,CLI,ANH3,ANH4,CY(I),ANCL2
0108             26 J = J + 1
0109                 PRINT 103
              C---->PPINT SECOND COPY OF OUTPUT:
0110                 PRINT 99, MO, NDAY, NYR
0111                 PRINT 102
0112                 PRINT 100, (MB(J), (C(J,I),I=1,11), J=1,NB)
0113                 PRINT 103
0114             98 FORMAT (3I3, 2E8.2, I3)
0115             99 FORMAT (1H1,20X, 'EXPERIMENT OF', 1X, I2, '/', I2, '/', I2,/)
0116            100 FORMAT (5X,I5,1P2E10.3,0PF10.3,1P8E10.3,/)
0117            101 FORMAT (I5,2F10.4,F6.2)
```

```
0116           102 FORMAT (5X,'BOTTLE',1X,'TOTAL CL2',1X,'TOTAL NH3',6X,'PH',6X,
                    C'HOCL',6X,'OCL-',7X,'CL2',7X,'CL-',7X,'NH3',6X,'NH4+',5X,'NH2CL',
                    C5X,'NHCL2',/)
0119           103 FORMAT (5X,'CL CONTAINING SPECIES IN PPM AS CL, NON-CL CONTAINING
                    CSPECIES IN PM AS N')
0120           301 FORMAT (10X,'SOMETHING IS WRONG, CHECK TCL')
0121           305 FORMAT (10X,'CX IS LARGER THAN TCL. PROGRAM TERMINATED.')
0122           303 CONTINUE
0123               STOP
0124               END
```

63

APPENDIX B

CALCULATION OF $V_{NO_3^-}$ (22)

CALCULATION OF $V_{NO_3^-}$ (22)

Percent ^{15}N enrichment = $100/(2R + 1)$ where R is the mean of the

28 peak height-29 peak height ratio, which is determined from the mass

spectra of the sample.

$V_{NO_3^-} = (A_f \cdot PN)/(A_i \cdot hr)$, where A_f is the difference between the

mean of the percent ^{15}N of the blanks and the percent ^{15}N of the sample,

PN is the concentration of particulate nitrogen, A_i is the percent ^{15}N

in the sample, and hr is time. $V_{NO_3^-}$ has units of micromoles nitrogen

taken up per liter per hour.

APPENDIX C

STANDARDIZATION OF PHENYLARSINE OXIDE

Standardization of Phenylarsine Oxide

A 0.100 $\underline{N}$ solution of sodium arsinite was prepared from 4.950 g of primary grade As_2O_3 dissolved in one liter of water containing 15 g NaOH. Carbon dioxide was then bubbled through the solution. The sodium arsinite was used to standardize a 0.1 $\underline{N}$ solution of iodine. The iodine solution was prepared from 40 g KI and 13 g resublimed iodine dissolved in one liter of water. The end points for the titration of 25.0 ml of iodine solution using starch as an indicator are given below.

TABLE XV

STANDARDIZATION OF IODINE SOLUTION

Sample	ml of Sodium Arsinite
1	24.16
2	24.18
3	24.15
average	24.16

Concentration of the iodine solution is 0.1305 N.

A 0.02812 $\underline{N}$ solution of iodine was obtained by placing 272.5 ml of

the standardized iodine solution in a one liter volumetric flask and

adding 25 g KI then diluting to the mark.

The phenylarsine oxide solution was prepared from 0.8 g C_6H_5AsO

powder in 15 ml of 0.3 $\underline{N}$ NaOH. Hydrochloric acid was added until a pH

of 6 to 7 was obtained. The phenylarsine oxide was standardized

against the 0.0282 $\underline{N}$ iodine solution. One-half milliliter of 0.0282 $\underline{N}$

iodine solution was placed in a flask containing 25 ml of distilled

water and titrated with the phenylarsine oxide solution using the

amperometric end-point detection apparatus. The titration data are

given below.

TABLE XVI

STANDARDIZATION OF PHENYLARSINE SOLUTION

ml Titrant	Voltage		
	Sample 1	Sample 2	Sample 3
0	1.02	1.00	1.05
1.00	0.93	0.94	0.96
2.00	0.86	0.84	0.87
2.30	0.67	0.64	0.67
2.40	0.58	0.53	0.57
2.42	0.41	0.39	0.40
2.43	0.34	0.35	0.33
2.44	0.34	0.33	0.33
2.45	0.34	0.33	0.33

The average volume of phenylarsine oxide is 2.43 ml. This gives a
phenyl oxide concentration of 0.00580 N. To obtain a 0.00564 N solu-
tion of phenylarsine oxide 2.84 ml of distilled water was added to 100
ml of the phenylarsine oxide to produce a 0.00564 N solution. One ml
of 0.00564 N phenylarsine oxide solution will equal 0.200 ppm of chlorine
in the chlorine unknowns.

VITA

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