

**BREAKPOINT CHLORINATION AS AN ALTERNATE MEANS  
OF AMMONIA-NITROGEN REMOVAL AT A WATER RECLAMATION PLANT**

by

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(ABSTRACT)

Numerous wastewater treatment processes are currently available for nitrogen removal or ammonia conversion to nitrate. Those that are economically feasible rely mostly on microbiological processes, which are only effective when the microorganisms remain in a healthy state. If a biological process upset was to occur, due to a toxic shock load or cold weather, it may result in a discharge of ammonia or total nitrogen into the receiving water body. The impact of such a discharge could have deleterious effects on aquatic life or human health. The main objective of the breakpoint pilot study was to define optimum breakpoint pilot plant operating conditions which could then be applied to the design of a full scale breakpoint facility and serve as an emergency backup to biological nitrification. A pilot study was built on site at the Upper Occoquan Sewage Authority's Regional Water Reclamation Facility in Centreville Virginia. Testing was conducted in two phases (I and II) over a two year period in order to determine the operating conditions at which the breakpoint reaction performed best. Tests were performed during Phase I to determine the optimum operating pH,

Cl<sub>2</sub>:NH<sub>3</sub>-N dose ratio, SO<sub>2</sub>:Cl<sub>2</sub> dose ratio, and the minimum detention time for completion of the breakpoint reaction. Other testing done during Phase I included several special studies; including examination of appropriate analytical methods for monitoring breakpoint reactions, and investigation of the breakpoint reaction by-product nitrogen trichloride. Phase II testing examined how varying breakpoint operating temperatures, varying influent ammonia concentrations, higher influent organic nitrogen concentrations, and higher influent nitrite concentrations influenced the performance of the breakpoint pilot operation.

Averages of data from operation at three different rapid mix pHs (7.0, 7.5, and 8.0) showed that pilot performance (i.e., ammonia oxidation) improved and the reaction was more stable at the higher operating pHs 7.5 and 8.0. Examination of dose ratios used during the study showed that the ideal operating ratios for this particular water was around 8:1 Cl<sub>2</sub>:NH<sub>3</sub>-N for the breakpoint reaction and 1.3:1 SO<sub>2</sub>:Cl<sub>2</sub> for the dechlorination reaction. Although detention times for completion of the breakpoint reaction varied with pilot influent temperature, it generally required around 30-35 minutes to reach ammonia concentrations of < 0.2 mg/L NH<sub>3</sub>-N at 8 -12 °C. Completion of the breakpoint reaction was found to be quickest at 20 °C (the highest water temperature tested at the pilot).

The tests of varying influent ammonia concentrations showed that although higher influent ammonia concentrations (11.0 mg/L) resulted in faster ammonia oxidation rates initially, the pilot operated better and had the same final performance results when the influent ammonia was lowered.

Increasing the organic nitrogen concentrations (~ 1.0 mg/L) in the pilot influent resulted in a slightly higher Cl<sub>2</sub>:NH<sub>3</sub>-N dose ratio needed to reach breakpoint, a higher SO<sub>2</sub>:Cl<sub>2</sub> dose needed to

dechlorinate, and resulted in the formation of numerous disinfection byproducts. Increasing the nitrite concentration in the pilot influent increased the chlorination dose requirement.

## *Acknowledgments*

I would like to reflect on how I got to this level of academia, as I originally had doubts about making it out of high school. Despite all of my attempts to prove him wrong, my father maintained complete confidence in me during my endeavor to become an adult. Throughout my life my father provided me with sound advise, inspiration to do better, trust, and friendship, he asked for nothing in return. My father was more of a factor in setting my life straight then he could ever know, and I wish I had completed this thesis before his passing. The place in my heart he filled, both as a father and as a friend, will always be empty - it is a painful feeling that doesn't seem to diminish with time. It was shortly after his passing that my disinterest in finishing this thesis became full blown. I feel I owe it to him to complete what I started, something he taught me from an early age.

I would like to thank my wife Jackie, for her continued encouragement and patience while I was obtaining a Masters Degree.

Special thanks are given to Dr. Thomas J. Grizzard who not only instigated me, but also presented me with the opportunity to obtain my masters degree, for that I will always be grateful.

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The success of the breakpoint pilot study can be attributed to the efforts of many talented individuals at UOSA and elsewhere. This thesis would not be complete without acknowledging those contributions.

Gib Ehalt - a virtual database of UOSA plant operations knowledge, experiences, and jokes.

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## *Table of Contents*

<b>INTRODUCTION.....</b>	<b>1</b>
Objectives .....	3
<b>LITERATURE REVIEW .....</b>	<b>5</b>
Breakpoint Chlorination .....	5
Chlorine Chemistry.....	8
Ammonia Chemistry .....	9
Chlorine-Ammonia Chemistry .....	10
Monchloramine .....	11
Dichloramine.....	12
Nitrogen Trichloride.....	13
Breakpoint Chlorination By-Products .....	15
NCl <sub>3</sub> .....	15
Disinfection By-products (DBPs) .....	15
Organochloramines .....	16
Chlorine Demand .....	16
End Products .....	16
Stoichiometry.....	17
Kinetics.....	17
Operating Parameters .....	18
pH.....	18
Dose Ratio .....	19
Mixing .....	19
Analytical Methods of Past Researchers .....	20
NH <sub>3</sub> Measurement.....	20

Cl <sub>2</sub> Speciation Measurements .....	20
<b>SPECIAL STUDIES</b> .....	21
Dye Studies.....	21
Cl <sub>2</sub> Demand.....	22
Interference Determination.....	24
Pilot Study Chlorine Residual Method Comparison .....	32
Cl <sub>2</sub> Speciation.....	32
Nitrogen Trichloride Analysis.....	36
Ammonia Nitrogen Analysis.....	39
Breakpoint Characterizations.....	42
<b>MATERIALS and METHODS</b> .....	48
Pilot Plant Design .....	48
pH Control.....	50
Ammonia Feed.....	50
Chlorine Feed.....	51
Sodium Bisulfite.....	51
Pilot Design Criteria (Phase I) .....	52
Pilot Design Criteria (Phase II).....	52
Duration.....	53
Pilot Plant Instrumentation .....	54
Analytical Methods .....	56
Pilot Plant Methods.....	56
Laboratory Methods.....	58
Contracted Laboratory Methods.....	59
Analytical Monitoring Program .....	60



<b>PHASE I - RESULTS and DISCUSSION.....</b>	<b>62</b>
<b>PHASE I – SUMMARY and CONCLUSIONS .....</b>	<b>78</b>
<b>PHASE II - RESULTS and DISCUSSION .....</b>	<b>80</b>
<b>PHASE II - SUMMARY and CONCLUSIONS .....</b>	<b>91</b>
<b>OVERALL CONCLUSIONS and RECOMMENDATIONS.....</b>	<b>93</b>
<b>REFERENCES.....</b>	<b>94</b>
<b>VITA.....</b>	<b>100</b>

## **APPENDICES**

The appendices referenced in this manuscript were intentionally left out at the request of the funding party. The appendices are however available on location at UOSA or via request to the Author and with approval of UOSA. All information in the appendices is in electronic format and can be sent via email or other means.

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## List of Figures

Figure 1.	Theoretical Breakpoint Curve.....	7
Figure 2.	Mixing characteristics of entire pilot plant .....	23
Figure 3.	DPD chlorine analysis of AWT effluent.....	25
Figure 4.	Amperometric analysis of AWT effluent.....	26
Figure 5.	Analysis for Total Chlorine Using Amperometric Instrumentation .....	28
Figure 6.	Analysis for Total Chlorine Using DPD Method.....	29
Figure 7.	Analysis for Free Chlorine Using Amperometric Instrumentation.....	30
Figure 8.	Analysis for Free Chlorine Using Amperometric Instrumentation.....	31
Figure 9.1.	DPD vs. Amperometric Analysis for Free Chlorine.....	35
Figure 9.2.	Amperometric Analysis for Total Chlorine .....	35
Figure 10.	$\text{NCl}_3$ Static Test Reactor .....	37
Figure 11.	Plot of $\text{NCl}_3$ Data from Reactor Studies .....	40
Figure 12.	Breakpoint Characterizations pH = 7.0.....	43
Figure 13.	Breakpoint Characterizations pH = 7.5.....	44
Figure 14.	Breakpoint Characterizations pH = 7.5.....	45
Figure 15.	Breakpoint Characterizations pH = 8.5.....	46
Figure 16.	Breakpoint Pilot Plant Schematic.....	49
Figure 17.	$\text{NH}_3$ Disappearance at pH 7.0, 7.5 and 8.0 runs .....	64
Figure 18.	Combined Chlorine Residual disappearance at pH 7.0, 7.5 and 8.0 .....	67
Figure 19.	Data Acquisition System Plot of $\text{Cl}_2$ Underfeed .....	69
Figure 20.	Data Acquisition System Plot of Loss of Breakpoint at pH 8.0.....	70
Figure 21.	Data Acquisition System Plot of Minimum $\text{Cl}_2$ Residuals @ pH= 7.0.....	72
Figure 22.	Data Acquisition System Plot of Minimum $\text{Cl}_2$ Residuals @ pH-8.0.....	73
Figure 23.	$\text{NH}_3$ Conc. vs. Time at Different Water Temperatures.....	81
Figure 24.	Combined Chlorine Residual vs. Time at Different Water Temps. ....	82
Figure 25.	$\text{NH}_3$ Disappearance vs. Time for Varying Influent $\text{NH}_3$ Conc.....	85
Figure 26.	$\text{NH}_3$ Conc. vs. Detention time for Increased $\text{NO}_2$ and ORG-N runs .....	88

## List of Tables

Table 1.	Temperature Dependency of $pK_a$ for HOCl.....	9
Table 2.	Temperature Dependency of $pK_b$ for Ammonia ( $NH_3$ ) .....	10
Table 3.	UOSA Lab Nitrogen Series Analysis .....	32
Table 4.	Data from UV Analysis of Samples from $NCl_3$ Reactor.....	41
Table 5.	Monitoring Program for Pilot Plant .....	60
Table 6.	Laboratory Analytical Monitoring Program.....	61
Table 7.	Pilot Plant Analytical Monitoring Program.....	61
Table 8.	Data Averages for the pH 7.0, 7.5 and 8.0 runs.....	63
Table 9.	UOSA Laboratory Averages for the pH 7.0, 7.5, and 8.0 runs.....	65
Table 10.	UOSA Laboratory Analysis of Pilot Plant Samples.....	76
Table 11.	Pilot Plant Averages for 8, 12, and 20 Degree C runs.....	83
Table 12.	Pilot Plant Averages for the 11.0, 6.0, and 2.0 mg/L $NH_3$ runs.....	86
Table 13.	Pilot and UOSA Lab Averages of $NH_3$ -N, $NO_2$ -N, and ORG-N runs .....	89

## ***INTRODUCTION***

Of the numerous processes for ammonia removal from or conversion in wastewaters, those that currently exist mostly rely on microbiological processes. These biological processes are most effective only when the microorganisms exist in a favorable environment. If loss of nitrification were to occur due to a toxic shock load or cold weather it could result in a discharge of ammonia into the receiving water body resulting in deleterious effects on aquatic life and potential for degrading of water quality.

The Upper Occoquan Sewage Authority (UOSA) Regional Water Reclamation Plant located in Centreville, Virginia, is one of the few plants in the United States which reclaims wastewater for indirect reuse in a potable water supply. After mixing and storage in the Occoquan Reservoir, the reclaimed water serves as a steady and reliable source of high quality drinking water for a system serving over  $10^6$  people in the Virginia suburbs of Washington D.C. The UOSA plant was designed for operational reliability and redundancy in order to maintain a high quality effluent under all circumstances. To this end, nitrification, selective ion exchange, and breakpoint chlorination processes have been provided for nitrogen management. Nitrification involves the conversion of ammonia to nitrate *via* microbiological processes. As with any biological process, nitrification relies on optimal environmental conditions to function properly. The Ion exchange process physically

removes ammonia by adsorption to clinoptilolite media in a filter bed arrangement. Once the clinoptilolite media is exhausted (as is evidenced when it won't adsorb any more ammonia) it is regenerated with a salt solution and placed back in service. Breakpoint chlorination involves the use of chlorine (in the form of gas or sodium hypochlorite solution) to chemically oxidize ammonia and convert it to nitrogen gas.

The UOSA plant is required to meet an average monthly TKN (Total Kjeldahl Nitrogen) limit of 1.0 mg/L. UOSA currently uses nitrification to meet this requirement. However, UOSA is also required to operate nitrogen removal facilities if the nitrate concentration exceeds 5.0 mg/L as  $\text{NO}_3\text{-N}$  in the vicinity of the downstream water treatment plant intake. This requirement, together with the possibility of a nitrification upset, results in a year round need for nitrogen removal at UOSA. Due to the significant lead-time needed to make the ion exchange process operational for ammonia removal (The UOSA ion exchange beds have been retrofitted to serve as post carbon filters), another means to quickly respond to a nitrification upset is needed. A breakpoint chlorination process may serve this need, as it relies on easily obtainable sodium hypochlorite to complete the conversion of ammonia to nitrogen gas.

Breakpoint chlorination has been practiced at wastewater plants as a physical-chemical process for removing ammonia on both a polishing and full scale basis. However, the process dynamics of a full scale breakpoint operation are poorly understood. Attempting to control the breakpoint process to produce an effluent free of ammonia nitrogen as well as undesirable byproducts has proven to be quite challenging. The purpose of this pilot study was to define breakpoint operating conditions that may

be encountered in a full-scale facility and to develop the control techniques that would provide consistent plant performance.

It is important to note that while this research is being conducted at a wastewater treatment plant, the quality of the UOSA effluent is more characteristic of a drinking water plant than that of a wastewater treatment plant. UOSA is required to comply with a very stringent discharge permit and thus constantly exceeds the quality of the receiving water stream into which it discharges. As a result of the high quality UOSA effluent the  $\text{Cl}_2:\text{NH}_3$  dose ratios needed to reach breakpoint during this study are lower than those that would typically be expected for a wastewater treatment plant. UOSA effluent is essentially void of chlorine demand, organics, and other constituents, which could create challenges during breakpoint operations at other plants, and result in an effluent quality that does not correlate well with that of this study. The results of this study are not likely to be repeatable with a wastewater that has not been processed to the same degree as UOSA.

## **Research Objectives**

### **Overall Objectives of this study were:**

Determine the process dynamics for real-time, continuous-flow breakpoint operations.

Define design criteria for a full-scale breakpoint facility.

Predict VPDES permit compliance.

Address safety issues.

## **Phase I**

### **Specific Objectives for Phase I were:**

Determine optimum chlorine to ammonia dose ratio.

Determine optimum reaction pH for the process

Determine reaction times and required detention times.

Investigate analytical methods for reliable measurement of parameters required for control of the breakpoint process.

Determine optimum  $\text{SO}_2:\text{Cl}_2$  dose ratio for dechlorination.

## **Phase II**

### **Specific Objectives for Phase II were:**

Determine effects of different influent water temperatures (8, 12 and 20 °C) on the performance of the breakpoint reaction.

Determine the effect of various influent ammonia concentrations (2.0, 6.0 and 11.0 mg/L  $\text{NH}_3\text{-N}$ ) on the breakpoint reaction.

Determine the effect of increased influent nitrite concentrations (~5.0 mg/L  $\text{NO}_2\text{-N}$ ) on the dose ratios required for breakpoint.

Determine the effect of increased influent organic nitrogen concentrations (~1.0 mg/L) on the breakpoint reaction.

Perform a special study to assess the potential for nitrogen trichloride formation during breakpoint operation.



## *Literature Review*

There has been limited research done on the breakpoint chlorination phenomenon. Initial research occurred in the first half of the century when breakpoint was a hot topic and drew the attention of researchers. The latter half of this century has seen little done in the way of research into breakpoint chlorination. With the exception of a few papers, mostly plant specific studies have been performed. There has, however, been a great deal of research done in the field of chlorine and chlorine-ammonia chemistry, as well as advances in the fields of chlorine and ammonia analysis. While this chapter will certainly review all obtainable research on breakpoint chlorination, it will also focus on research done in the field of chlorine-ammonia chemistry, as it pertains to the breakpoint reaction.

### **Breakpoint Chlorination**

The physical-chemical process of ammonia oxidation with chlorine has been practiced in the water treatment field for over 50 years. As early as the 1920s superchlorination was used as a successful means of controlling taste and odors in water treatment plants. In the 1930s an unexplained phenomenon was being observed at water treatment plants using higher than normal chlorine dosages. These events prompted research into the chlorination reactions occurring at water treatment plants. Among the first researchers to explain these chlorine reactions Griffin (16) used the term breakpoint to describe the point where chlorine and ammonia concentrations were simultaneously minimized.

The breakpoint reaction is defined as the chlorination of a water containing ammonia resulting in an initial increase in combined chlorine residual, followed by a decrease in the combined chlorine residual along with ammonia concentrations, followed by an increase in free chlorine residual and near complete removal of ammonia as nitrogen gas. Fig. 1 shows a hypothetical breakpoint curve for a water with a dose requirement of 9:1 Cl : NH<sub>3</sub> (20). Initial research efforts into the mechanism of the breakpoint reaction are attributed to Calvert (4), and later studies by Griffin and Chamberland (17), and Rossum (34). Ensuing research by others (32,41,43) has led to an understanding of the stoichiometry and kinetics associated with the breakpoint process. More recently, a comprehensive study of the kinetics of breakpoint chlorination was performed by Saunier and Selleck (36). The goal of their work was to develop a mathematical model, derived from laboratory observations, which would provide “a rational basis for the design and operation of the breakpoint process in order to achieve predictable ammonia removal”(36). Unfortunately, past research yielded little or no insight into the problem of successfully controlling the breakpoint process in a full-scale wastewater treatment plant. Although Saunier and Selleck (36) performed comprehensive pilot study work, the results were never incorporated into a full-scale plant application. Pressley *et al.* (33) performed extensive pilot study research in order to provide design criteria for a full scale breakpoint operation at the Blue Plains wastewater treatment plant in Washington, D.C.. Atkins *et al.* (1) performed an extensive pre-design pilot study to provide information for full- scale breakpoint operations at the Owosso wastewater treatment plant in Michigan. The engineering firm of Camp, Dresser & McKee (5) also performed bench scale

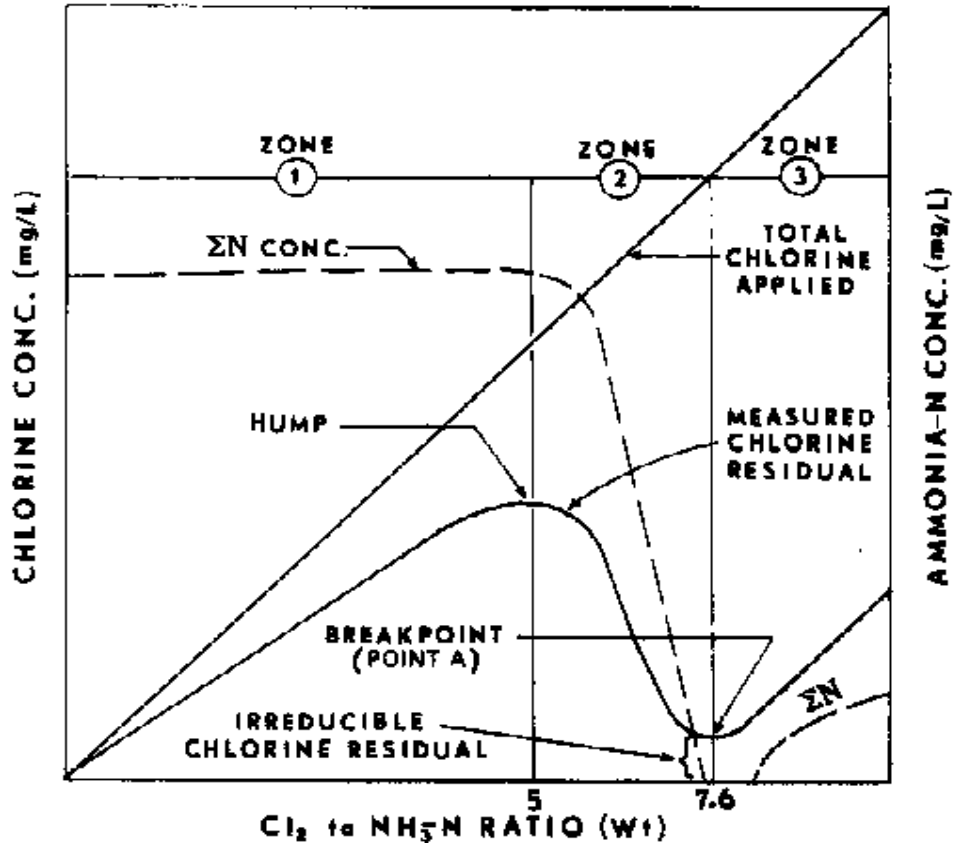


Figure 1. Theoretical breakpoint curve. (Zone 1 is associated with the reactions of chlorine and ammonia to form Monochloramine; Zone 2 is associated with an increase in dichloramine and the disappearance of  $\text{NH}_3$ ; Zone 3 is associated with the appearance of free chlorine after the breakpoint)(44).

breakpoint testing before construction of full scale facilities at the Lower Potomac Pollution Control Plant in Lorton Virginia. However, no matter how successful the pilot studies (1,5,33) were, or how much information they yielded, none have been able to use the pilot information to successfully control a full scale breakpoint facility.

## Chlorine Chemistry

### Chlorine Hydrolysis

Sodium hypochlorite hydrolyzes rapidly in water according to the following reaction:



The formation of HOCl *via* the above reaction is essential before the initiation of the breakpoint reaction. Because hypochlorous acid is a weak acid it undergoes only partial dissociation as follows:



At pH values between 6.5 and 8.5, the above reaction is incomplete and both species are present to some degree. The extent of the above reaction can be estimated from the following equilibrium expression:

$$K_a = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} \quad (1-3)$$

Dissociation of HOCl in water has been measured by several investigators and has been shown to be temperature dependant. The following are hydrolysis constant data published by Morris (27):

Table 1 Temperature Dependency of pK<sub>a</sub> for HOCl

Temperature °C	0	5	10	15	20	25	30
----------------	---	---	----	----	----	----	----

pK <sub>a</sub>	7.82	7.75	7.69	7.63	7.58	7.54	7.49
-----------------	------	------	------	------	------	------	------

These values are derived from the following equation) (27):

$$pK_a = \frac{3000}{T} - 10.0686 + 0.0253T \quad (1-4)$$

where T = 273 + degrees Celsius.

### **Ionic Strength**

Ionic strength can play a role in the dissociation of hypochlorous acid. According to White (44) waters with higher TDS (Total Dissolved Solids) have stronger forces for molecular dissociation than low TDS waters. Hence, reclaimed wastewater (TDS > 400 mg/L) has a higher potential to dissociate molecules than a ground or surface water (TDS < 400 mg/L).

### **Ammonia Chemistry**

The presence of ammonia in wastewater is due in most part to the hydrolysis of urea to the ammonium ion at the pH values (7.0-7.5) typically found in raw domestic wastewater. The ionization reaction for the ammonium ion is:



Dissociation constants for ammonia published by Bates and Pinching (3) are summarized below:

Table 2 Temperature Dependency of pK<sub>b</sub> for Ammonia (NH<sub>3</sub>)

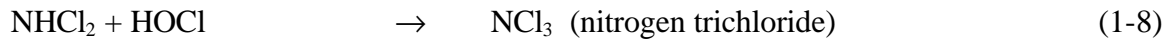
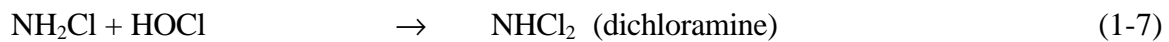
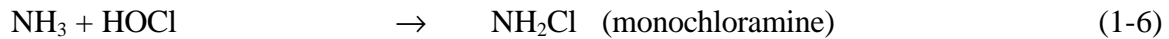
Temperature °C	0	5	10	15	20	25	30
pK <sub>b</sub>	10.08	9.90	9.73	9.56	9.40	9.25	9.09

Data from the above table show that one is very unlikely to find significant NH<sub>3</sub> at the pH values encountered during normal breakpoint chlorination operations (pH << 9.0).

### Chlorine-Ammonia Chemistry

Numerous studies and reviews have been done in the field of chlorine-ammonia chemistry (42-45).

From these studies, the following generalized reaction scheme is accepted for chloramine formation:



The chloramine composition in solution has been shown to be pH dependent (10,31,38). Morris (29) gives the following information on the chloramine formation pH dependency:

- at pH > 7.5, monochloramine is the dominant chloramine species
- as pH decreases from 7.5, dichloramine becomes the dominant chloramine species
- increases in the chlorine to nitrogen dose ratio results in corresponding increases of nitrogen trichloride, but only when the pH is < 7.4.

## Monochloramine

Monochloramine is very soluble in water and is prone to decomposition when exposed to light and heat (37).

### NH<sub>2</sub>Cl Chemistry

Polarity of the N-Cl bond in chloramine is very low (37). It has been shown that the N-Cl bond is polarized differently by various reactants (19), hence the more negative end may be the nitrogen in one case and the chlorine in another. The formation reaction is:



Numerous studies of this reaction rate have been performed (23,25,43). As recently as 1983, Morris and Isaac (25) concluded (based on research from all previous studies) that this reaction is elementary and has a rate constant of  $6.6 \times 10^8 \exp(-1510/T) \text{ M}^{-1} \text{ sec}^{-1}$ .

### Equilibrium

It has been determined that the monochloramine reaction does achieve equilibrium (8). Numerous researchers (8,14,15) have reported dissociation constants for monochloramine, none of which are in very good agreement.

### Dichloramine

Dichloramine occurs in solution only. The nitrogen-chlorine bond in dichloramine should be even less polar than in the case of monochloramine due to the additional chlorine atom bound to the nitrogen, thereby increasing the electronegativity of the latter (37). This theory is substantiated by data that show the solubility of dichloramine is greater in nonpolar organic solvents (27).

### **NHCl<sub>2</sub> Chemistry**

Research by Chapin (7) concluded that production of dichloramine was a direct result of excess chlorination of ammonia in the pH range of 4.4 to 8.5, and that at pH 4.5 to 5.0 dichloramine was the sole product. The formation reaction is:



Several researchers (23,25,29), have determined estimates of the rate constant for dichloramine. Based on the analysis of past research, as well as their own, Morris and Isaac (25) derived a composite forward rate constant of  $3.0 \times 10^5 \exp(-2010/T) \text{ M}^{-1}\text{sec}^{-1}$ .

### **Equilibrium**

Stating the equilibrium constant as:

$$K = \frac{[\text{NHCl}_2]}{[\text{NH}_2\text{Cl}][\text{HOCl}]} \quad (1-11)$$

The reciprocal of K (from above) was estimated to be about 25 times larger than that found for the corresponding monochloramine equilibrium (14). Many other researchers have estimated this



constant, the most recent being Morris and Isaac (25) who (based on all available research at the time) estimated the reciprocal of K for dichloramine to be  $2.2 \times 10^{-9}$  M in fresh water at 25 °C.

Conflicting estimates of the acid dissociation constant of Dichloramine have been presented in the literature :

$pK_a \cong 7$  (Jolly, 21)

$pK_a \cong 8$  (Morris, 28)

$pK_a \cong 13$  (Hand *et al.*, 18)

Although the equilibrium constant estimated by Morris was confirmed by the theoretical calculations of Jolly, dichloramine could not be detected even at very high pH values in research done by Hand. This absence of dichloramine led Morris to postulate that dichloramine must dissociate rapidly (28).

### **Nitrogen Trichloride**

Nitrogen Trichloride was first discovered in 1811 from the action of chlorine on a solution of ammonium chloride by Dulong, who lost an eye and three fingers as a result of an explosion. Dulong (11) determined the formula  $NCl_3$  for the yellow explosive oil. Further early research (24) showed that the thick oily  $NCl_3$  would explode violently when heated to 93 °C, when exposed to strong light, or brought into contact with a number of other substances. Nitrogen trichloride is sparingly soluble in water and is known to exert a high vapor pressure. These factors together result in  $NCl_3$  being easily stripped from water (24).

## **NCl<sub>3</sub> Chemistry**

The formation reaction for nitrogen trichloride is:



Several researchers have presented rate constants for the above reaction (25,32,35). Morris and Isaac (25) based their rate constant on all research available at the time of publication and recommended a rate constant of  $3.0 \times 10^5 \exp(-3420/T) \text{ M}^{-1}\text{s}^{-1}$  ( $3.2 < \text{pH} < 4.5$ ) for fresh water.

The decomposition reaction for nitrogen trichloride is:



The rate of nitrogen trichloride decomposition has been shown to be first order as a function of time (35). Kumar (22) demonstrated that NCl<sub>3</sub>, in the presence of excess hypochlorous acid, decomposed to either HOCl or was otherwise lost through oxidation/reduction. Eqs. 1-12 and 1-13 demonstrates that NCl<sub>3</sub> should be quite stable in the presence of excess chlorine and this is explained by the results of Kumar (22), who witnessed a slower rate of decomposition of NCl<sub>3</sub> than previous researchers.

## **Breakpoint Chemistry**

### **By-Products**

## **NCl<sub>3</sub>**

While nitrogen trichloride (NCl<sub>3</sub>) is formed from the above reaction (eq. 1-13), it is generally considered to be an intermediate product in breakpoint chlorination, even though it exists long enough to eventually revert to free ammonia after dechlorination. Data from pilot study work by Pressley (33) showed that at a pH range of 6-8 NCl<sub>3</sub> increased as the amount of free chlorine increased beyond the breakpoint. Data from the same study showed an increase in NCl<sub>3</sub> with decreasing pH. Saunier and Selleck showed an increase in NCl<sub>3</sub> when the chlorine to nitrogen dose ratio increased (36). It was also noted that NCl<sub>3</sub> formed early in the breakpoint reaction, and, once formed, it was very stable in the presence of free chlorine over time.

## **Disinfection By-Products (DBPs)**

At the time of this research there had been no known research to determine the which if any disinfection by-products were being created during breakpoint chlorination. While not the main focus of this research due to time and funding limitations, DBP formation potential from breakpoint reactions will be addressed.

## **Organochloramines**

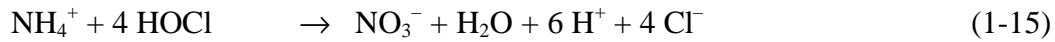
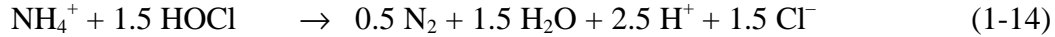
Wastewaters containing organic nitrogen, in addition to ammonia nitrogen, can create a variety of problems for breakpoint chlorination operations. Taras (39,40) categorized the source of chlorine consuming nitrogenous compounds as: ammonia, amino acids, and proteins. The formation of organochloramines in water during chlorination is well documented, (2,32,39,40,45). Griffin (17) found that waters containing both ammonia and organic nitrogen did not display a large dip in the breakpoint curve as compared to waters containing only ammonia. Organochloramines have also been identified as interfering compounds in chlorine residual determinations (44).

## **Chlorine Demand**

The bulk of the research on chlorine demand has been related to chlorination of potable waters. Feben and Taras (12,13) found a definite relationship between chlorine demand and the complexity of the organic nitrogen compounds found in the city of Detroit water supply. Pilot study work by Pressley *et al.* (33) correlated the level of pretreatment of the wastewater to the chlorine-to- ammonia ratio required to reach breakpoint. In their studies, water receiving high levels of treatment, e.g. waters with lower concentrations of organics present required lower Cl:NH<sub>3</sub>-N dosages to reach the breakpoint, while all other factors were constant (33).

## **End Products**

The end products of the breakpoint reaction were found to be primarily nitrogen gas (N<sub>2</sub>) and secondarily nitrate (NO<sub>3</sub><sup>-</sup>) (32,33,36). Attempts were made by Pressley *et al.* (33) to isolate N<sub>2</sub>O, NO, and NO<sub>2</sub> but these proved unsuccessful. The following reaction scheme is given for the formation of N<sub>2</sub> and NO<sub>3</sub><sup>-</sup> (44):



### **Stoichiometry**

The weight ratio of chlorine to ammonia required to reach the breakpoint, assuming  $\text{N}_2$  is the major end product, is 7.6:1 or, on a molar basis, 1.5:1. Research by Wei and Morris (41) indicated that the stoichiometric ratio of the breakpoint reaction was not affected by pH in the 6.7 - 7.2 range. This was in agreement with earlier studies (16,17). In more recent studies by Saunier and Selleck (36) the ratio of moles of chlorine reduced : moles of ammonia N oxidized increased with increasing contact time, and with increasing chlorine-to-ammonia dose ratio. The data agreed with previous studies by Wei and Morris (41). Pressley (33) showed that chlorine-to-ammonia dose ratios varied from approximately 8:1 to 10:1 for the waters tested in his studies. The dose ratio required was attributed directly to the extent of pretreatment the water received, with the more highly treated water requiring a lower dose ratio of 8:1. Saunier and Selleck (36) conducted studies with both tap water and tertiary effluent. They found higher chlorine-to-ammonia ratios were required to reach the breakpoint in the tertiary effluent than in tap water, and attributed this result to the oxidation of organics present in the tertiary treated water.

### **Kinetics**

The rate at which the overall breakpoint reaction proceeds to completion can be measured by combined chlorine concentration disappearance over time. The breakpoint reaction rate may be affected by temperature, pH, and initial ammonia nitrogen concentration. Studies by Wei and Morris

(41) showed a significant temperature effect on the breakpoint reaction with activation energies ranging from 7.8 kcal/mole to 12.85 kcal/mole. Data from these studies also showed a direct relationship between reaction stream temperature and persistence of combined chlorine residuals. Decreasing temperatures caused longer reaction times. Data from Saunier and Selleck (36) showed faster reaction rates as pH increased. The optimum reaction rates occurred between pH 7.0 and 8.0. Wei and Morris (41) noted that the most important effect of pH on breakpoint was how it affected the transient state of  $\text{NHCl}_2$ . As the pH dropped, they noted a decrease in the rate of decomposition of  $\text{NHCl}_2$  and hence slower overall breakpoint reaction rates. According to the proposed mechanism by Wei and Morris (41), the formation of  $\text{NHCl}_2$  is a second order reaction while its decomposition is first order. Based on this proposal they concluded that the maximum  $\text{NHCl}_2$  concentration should occur sooner and have a larger magnitude when the initial reactant ( $\text{NH}_3\text{-N}$ ) concentration is increased. As a consequence, the rate of decrease of  $\text{NHCl}_2$  and total chlorine would also be expected to increase with increased reactant concentration. The experimental data collected of Wei and Morris confirmed an increase in the breakpoint reaction rates with increases of initial ammonia concentration (41). Saunier and Selleck (36) observed a reaction rate increase by an order of magnitude when operating breakpoint at higher initial ammonia concentrations.

## **Operating Parameters**

### **pH**

The ideal operating pH for breakpoint is thought to lie somewhere between pH 7.0 and 8.0 (30,33,36). However, no research could be found that examined the effect of significant pH variations on the breakpoint reaction. Studies by Wei and Morris (41) noted that the most important

effect of pH on breakpoint in the ranges they investigated, pH 6.7 to 7.2, was that as the pH decreased the breakpoint reaction rate decreased.

Pressley *et al.* (33) noticed increases in  $\text{NO}_3$  as the pH increased. In the same study it was shown that after the breakpoint, the formation of  $\text{NCl}_3$  increased as the pH of the wastewater decreased. Contrary to these findings, Saunier and Selleck (36) found that  $\text{NO}_3$  and  $\text{NCl}_3$  concentrations were not as pH dependant as reported by Pressley *et al.*(33). Saunier and Selleck (36) also found that the oxidation of organic nitrogen occurred faster at pH values below 7.5.

### **Dose Ratio**

It has been observed in studies that as the chlorine to ammonia ratio exceeds the stoichiometric value of 7.6:1, the formation of  $\text{NCl}_3$  increases (36). Pressley *et al.* (33) also found that concentrations of  $\text{NCl}_3$  increased as the chlorine to ammonia dose ratio increased beyond the stoichiometric value needed for breakpoint. Other data (32,33) suggest that  $\text{NO}_3$  concentrations may also increase as the chlorine to ammonia ratio is increased. Saunier and Selleck's data (36) indicate that  $\text{NCl}_3$  was converted to  $\text{NO}_3$  in the presence of free chlorine and absence of significant concentrations of other chlorine species.

### **Mixing**

Initial mixing conditions in the breakpoint chamber may effect the reaction rate of the breakpoint process due to reactant stream segregation occurring between the chlorine and wastewater. Trial full-scale breakpoint tests conducted at the Tahoe Truckee plant in California indicated that proper initial mixing was very important in achieving the desired reactions within the breakpoint vault (10).

## **Analytical Methods of Past Researchers**

### **NH<sub>3</sub> Measurement**

The need for a fast, reliable, and accurate method of ammonia determination is critical for initial start-up and the subsequent monitoring of breakpoint process performance. Of the methods available for ammonia analysis, unfortunately none have proven to be foolproof for accurate breakpoint ammonia analysis. Available methods for ammonia analysis in wastewater include: Nesslerization method, Phenate method and, Ammonia selective electrode (38).

### **Cl<sub>2</sub> Speciation Measurements**

There is also a need for quick and accurate free and combined chlorine residual measurements. Reliable residual data are required to monitor and adjust chlorine dosages for controlling the process near the breakpoint. Of the methods available, the DPD (N,N-diethyl-p-phenylenediamine) method (31,38) was most widely used by previous investigators (1,33,36,38,41). Although both are subject to interference, recent research has shown that DPD and Amperometric methods are the most appropriate techniques for free available chlorine measurement (20). Available methods for free and total chlorine residual measurement include: Amperometric, DPD Ferrous Titrimetric, and DPD Colorimetric methods (38). Analytical measurement of NCl<sub>3</sub> has proven to be difficult and cumbersome for past researchers. Pressley *et al.* (33) found poor reproducibility in measuring NCl<sub>3</sub> with the DPD-FAS method, and as a result opted to use the more sophisticated and time consuming method of extraction in CCl<sub>4</sub> and subsequent spectrophotometric measurement. Saunier and Selleck (36) also found poor reproducibility with the DPD-FAS method for NCl<sub>3</sub> measurement, but used it anyway due to the high cost and time-consuming nature of the CCl<sub>4</sub> extraction alternative.



## *Special Studies*

In order to understand fully the factors affecting the performance of the pilot study as a whole, it was necessary to conduct a series of "special studies". These studies were designed to address questions specific to the UOSA breakpoint pilot study, and could not be answered from either the literature or outside sources.

### **Dye Studies**

The following summary is given for the Pilot Plant Dye Studies. A comprehensive discussion is presented in Appendix A.

Fluorescent dye studies were performed in order to evaluate and quantify the mixing characteristics and detention times associated with the pilot plant reaction tanks. These tests were also designed to determine what effect the sample withdrawal for on-line instruments would have on the system detention times. Slug load tests were performed on the influent head tank, rapid mix reactors, contact tanks, and the effluent wet well. A slug load test was also used to evaluate the mixing characteristics and detention time of the system as a whole.

Rhodamine dye was diluted and injected into each basin and the effluent was monitored with a Turner Designs fluorometer with a continuous flow-through cell. An Esterline-Angus strip chart recorder was used to record all data output from the fluorometer. A positive displacement pump was used to deliver the sample to the fluorometer. After injection of the dye, the test continued until the effluent fluorescence was less than 10% of the maximum peak fluorescence for that basin.

## **Conclusions**

The pilot tanks performed well individually with respect to complete mix characteristics. The system as configured, with three completely mixed contact tanks in series, exhibited significant plug flow tendencies (Fig. 2). However, the three complete mix contact tanks in series provided more mixing and dispersion than was expected. The on-line chlorine analyzers did not have a significant effect on basin or system detention times in the pilot configuration because the analyzers withdrew from the 30 minute contact tank.

## **Cl<sub>2</sub> Demand**

Chlorine demand is defined as the difference between the amount of chlorine added to a water and the amount of chlorine (free and combined) remaining after a specified contact time. Special investigations were performed to determine the typical chlorine demand of UOSAs AWT (Advanced Waste Treatment) effluent (see Appendix B for a more comprehensive discussion). Two chlorine residual methods were used for this study: 1) Amperometric Titration (Standard Method 4500-Cl D), and 2) Hach's Accuvac Colorimetric DPD Method (modified Standard Method 4500-Cl G).

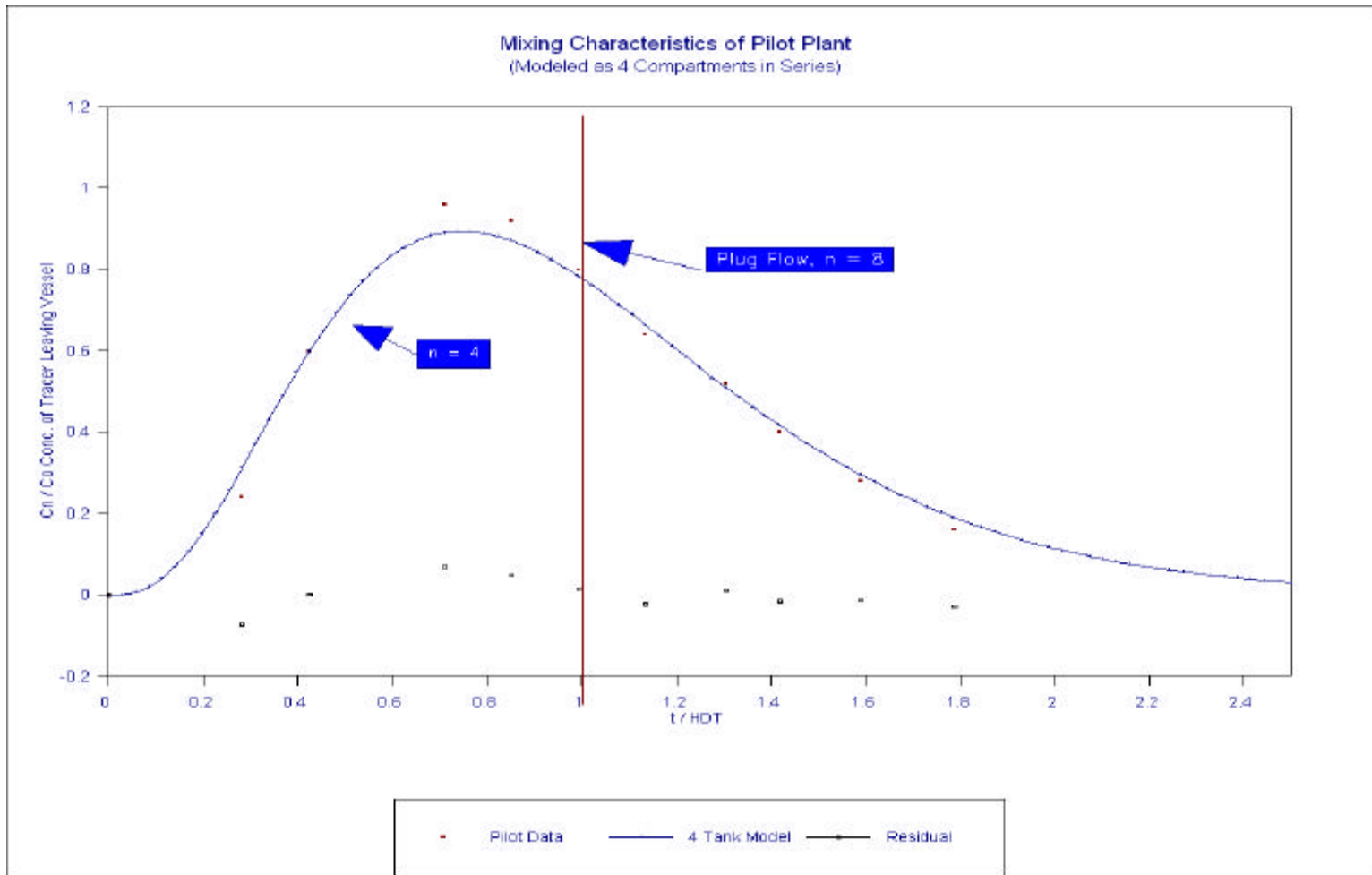


Figure 2. Mixing characteristics of entire pilot plant

## **Results and Discussion**

Results of the Cl<sub>2</sub> Demand study are presented in Figures 3 and 4. Due to the high degree of treatment associated with UOSA AWT effluent, the ammonia-N, organic-N and other oxidizable organic concentrations in the water were expected to be minimal. This was reflected in the small chlorine demand that was found during this study. Minimal chlorine demand equates to reduced chlorine feed rates to achieve breakpoint as well as reduced dosing rates to achieve disinfection of the UOSA plant effluent.

## **Conclusions**

Chlorine demand for the AWT effluent tested was in the range of 0.2 to 1.0 mg/L after 30 minutes of contact time, with no ultraviolet exposure.

## **Interference Determination**

Laboratory tests were conducted to quantify the degree of interference that organic chloramines would impart to chlorine analyses of the same water. A more comprehensive discussion can be found in Appendix C.

## **Results and Discussion**

Parallel tests were run, using two fundamentally different methods, in an attempt to quantify any interference organic chloramine might impart in the measurement of residual chlorine species in

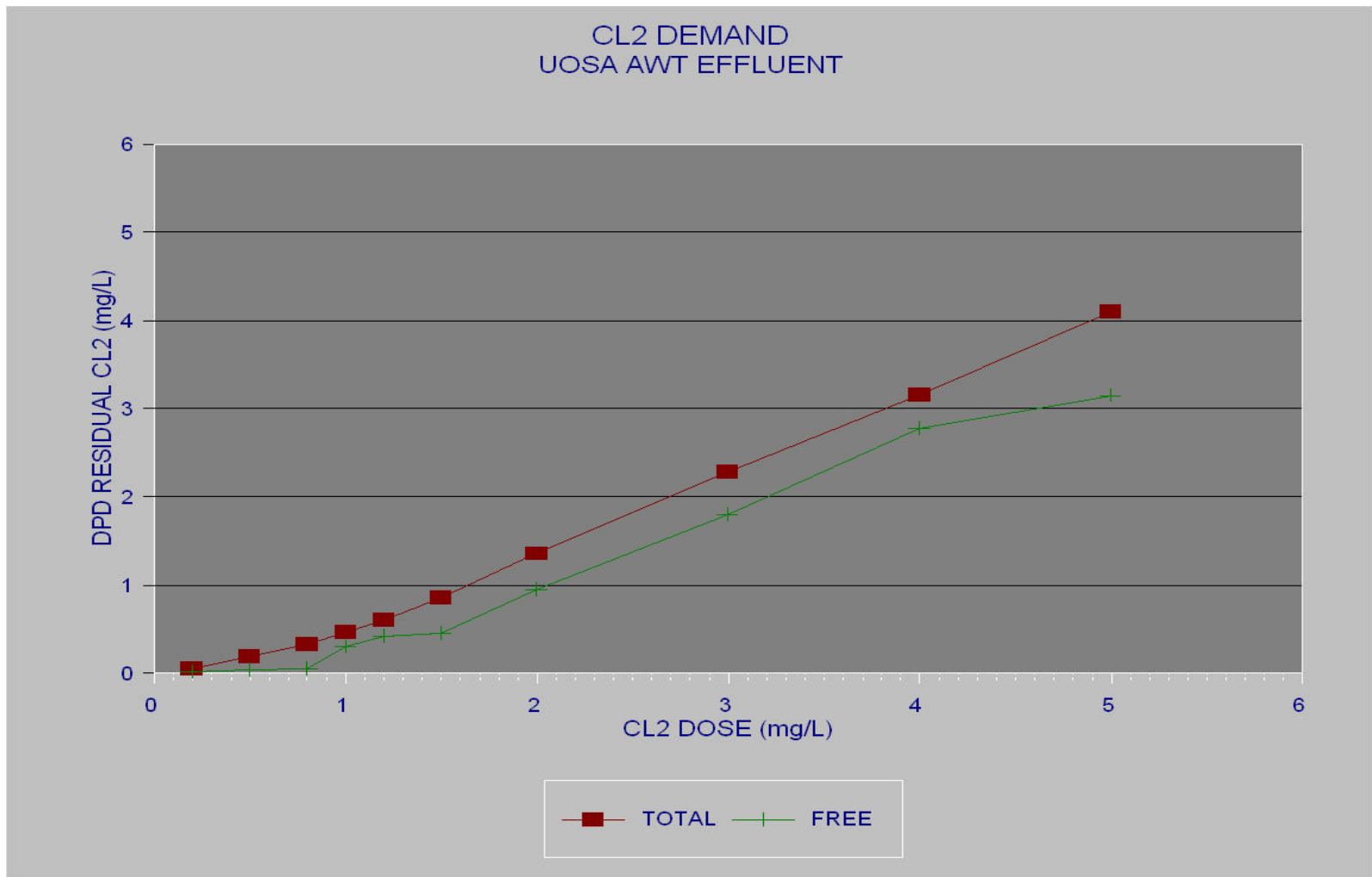


Figure 3. DPD chlorine analysis of AWT effluent

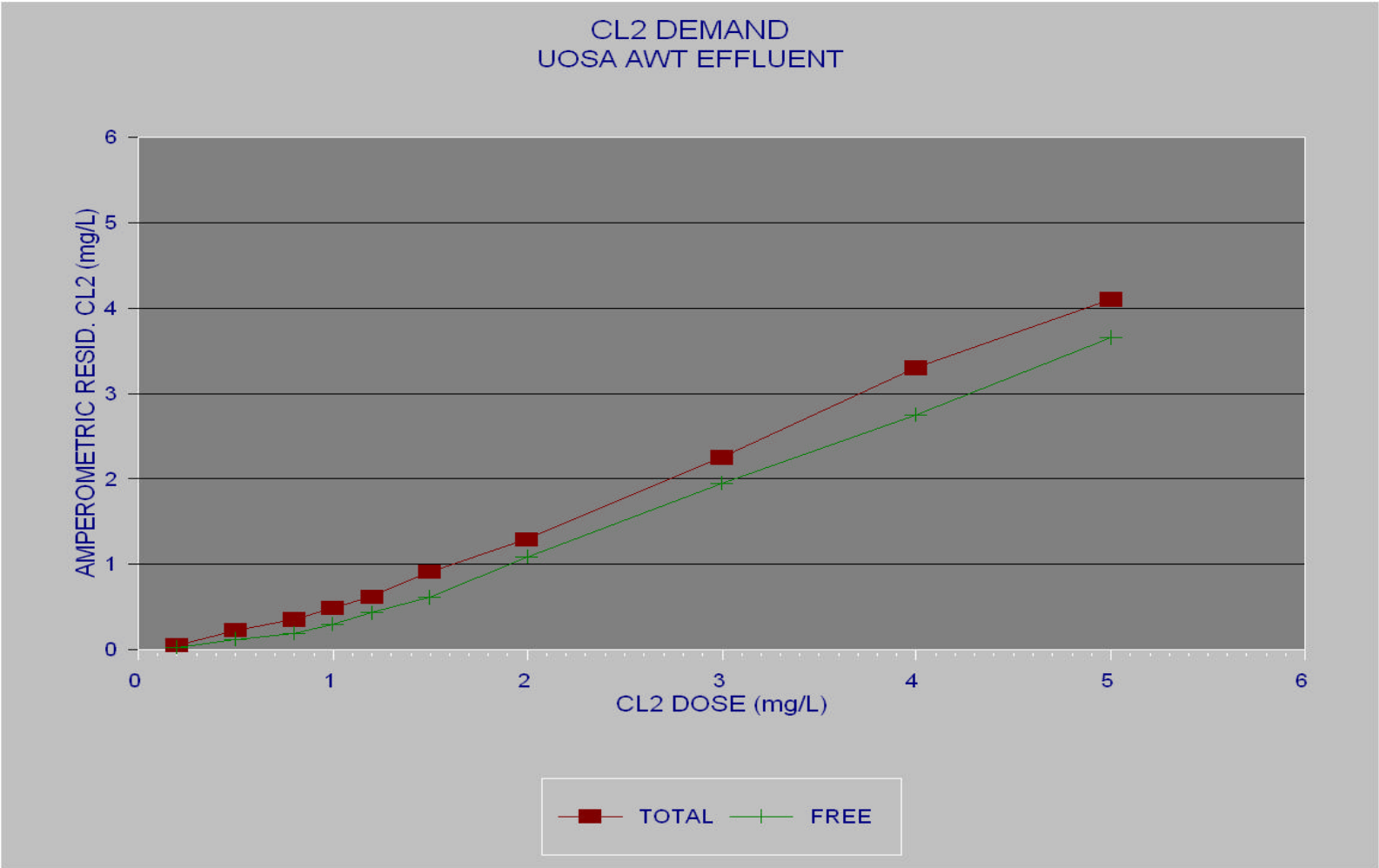


Figure 4. Amperometric analysis of AWT effluent

water. The analytical results of both methods correlated very well, as indicated in Figures 5 through 8. Laboratory results for the Nitrogen series ( $\text{NH}_3$ , TKN,  $\text{NO}_2$ ) run on each sample type (1 through 5) are summarized in Table 3. The close correlation of results from the interference testing indicate that analyst flexibility and method preference is the major factor in determining which analytical method will provide the most consistent results for assessing the chlorine content of water in order to determine breakpoint dosages needed.

### **Conclusions**

- 1) At the chlorine dosages and organic nitrogen (org-N) concentrations of 0.4 mg/L used in the study, organic chloramine interference with the free chlorine residual measurement using either the amperometric or Hach DPD colorimetric methods was negligible
- 2) At the chlorine dosages and org-N concentrations of 0.4 mg/L used in the study, organic chloramine interference with the combined chlorine residual measurement using either the amperometric or the Hach DPD colorimetric method is not sufficient to cause a problem with operating the breakpoint process.
- 3) Operating the breakpoint process with a combined chlorine residual greater than 1 mg/L after 30 minutes of contact time will minimize any interference in chlorine measurements from organic chloramines at the concentrations tested.
- 4) The results of the amperometric and Hach DPD colorimetric methods were very close except at residuals greater than 2 mg/L. At residuals higher than 2 mg/L dilution was required for the Hach DPD method. Dilution error may have been the reason that the two methods diverge at higher residuals.

### BREAKPOINT PILOT TESTING INTERFERENCE DETERMINATION

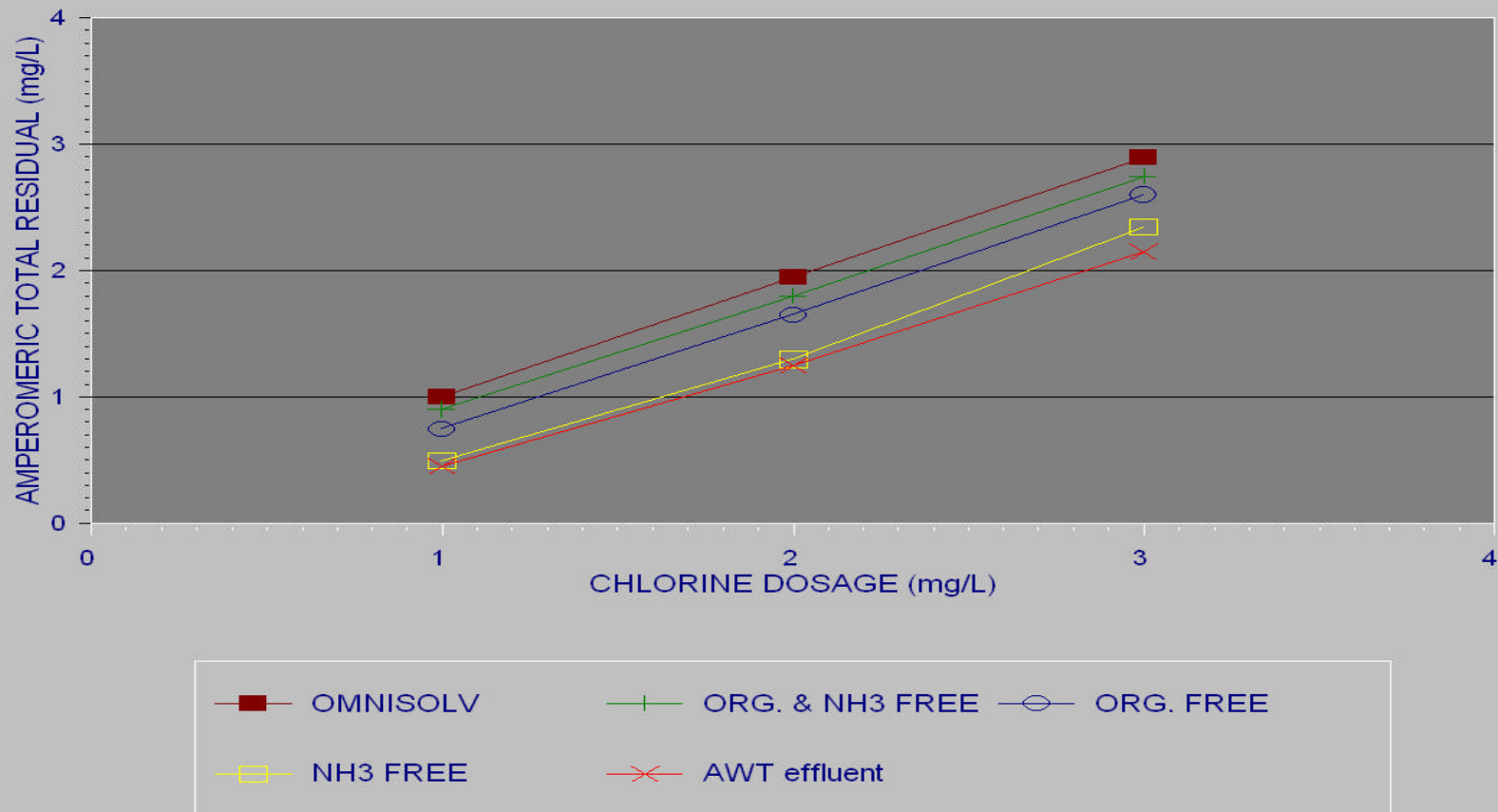


Figure 5. Analysis for Total Chlorine Using Amperometric Instrumentation



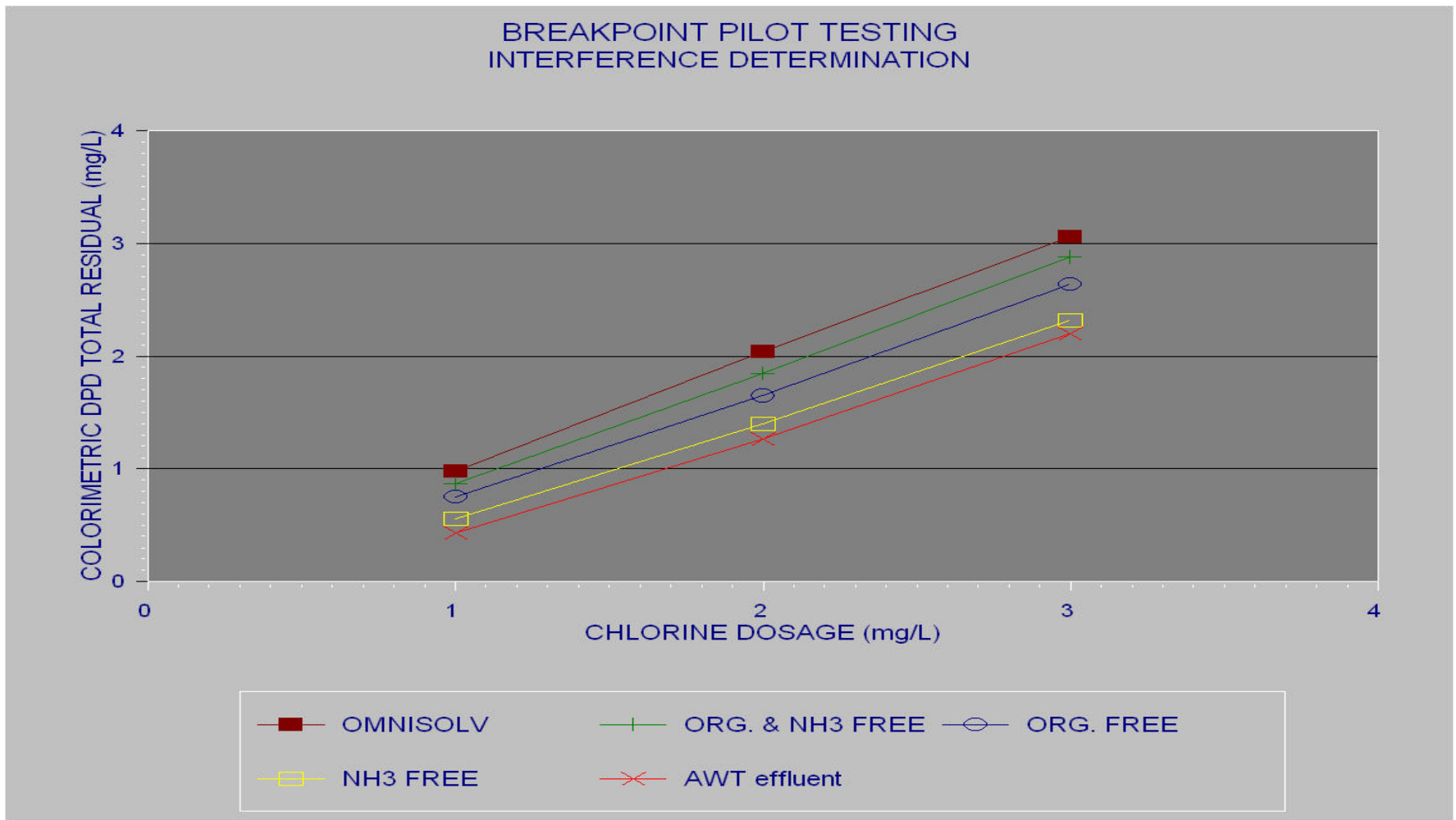


Figure 6. Analysis for Total Chlorine Using DPD Method

BREAKPOINT PILOT TESTING  
INTERFERENCE DETERMINATION

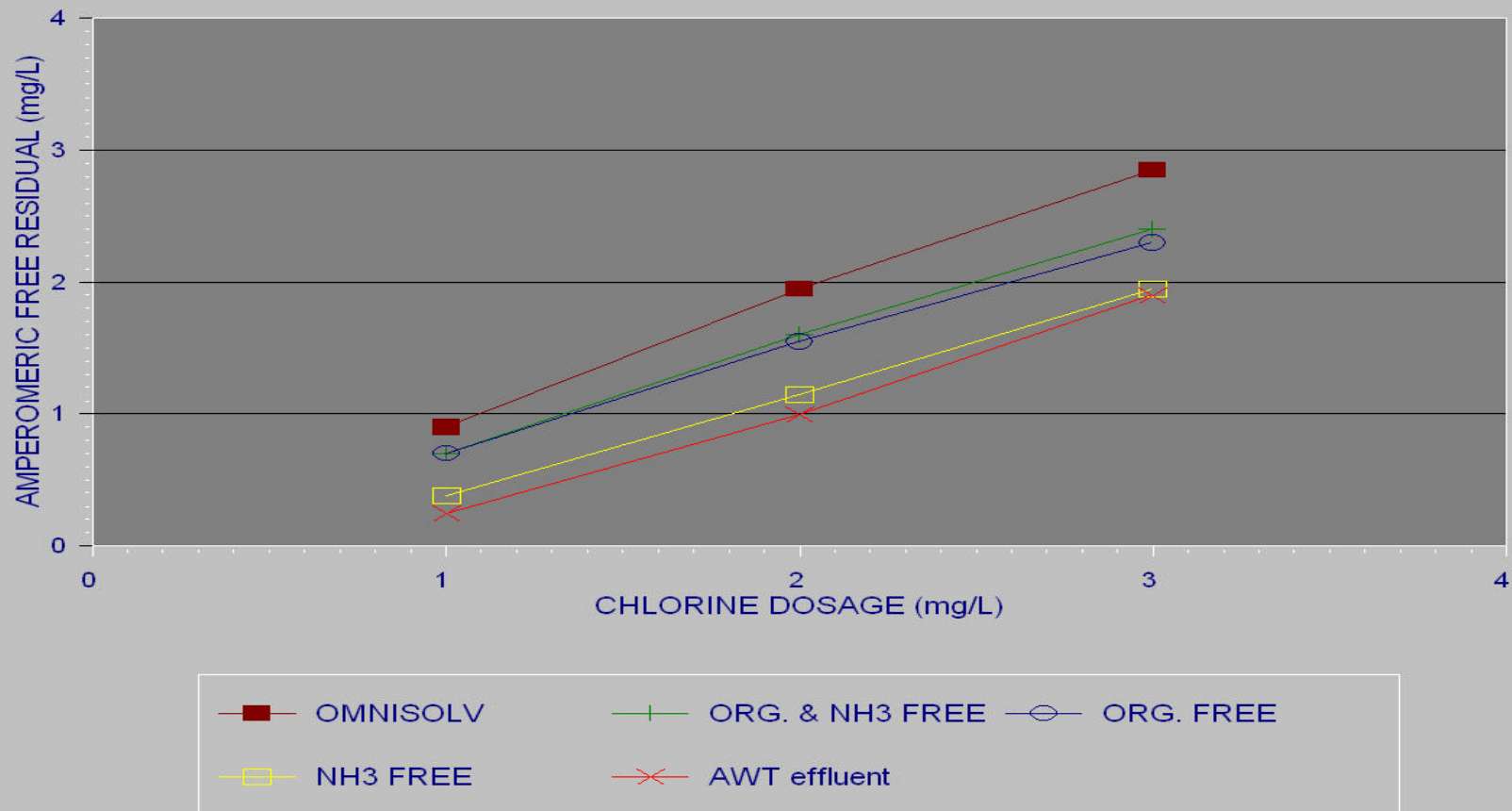


Figure 7. Analysis for Free Chlorine Using Amperometric Instrumentation

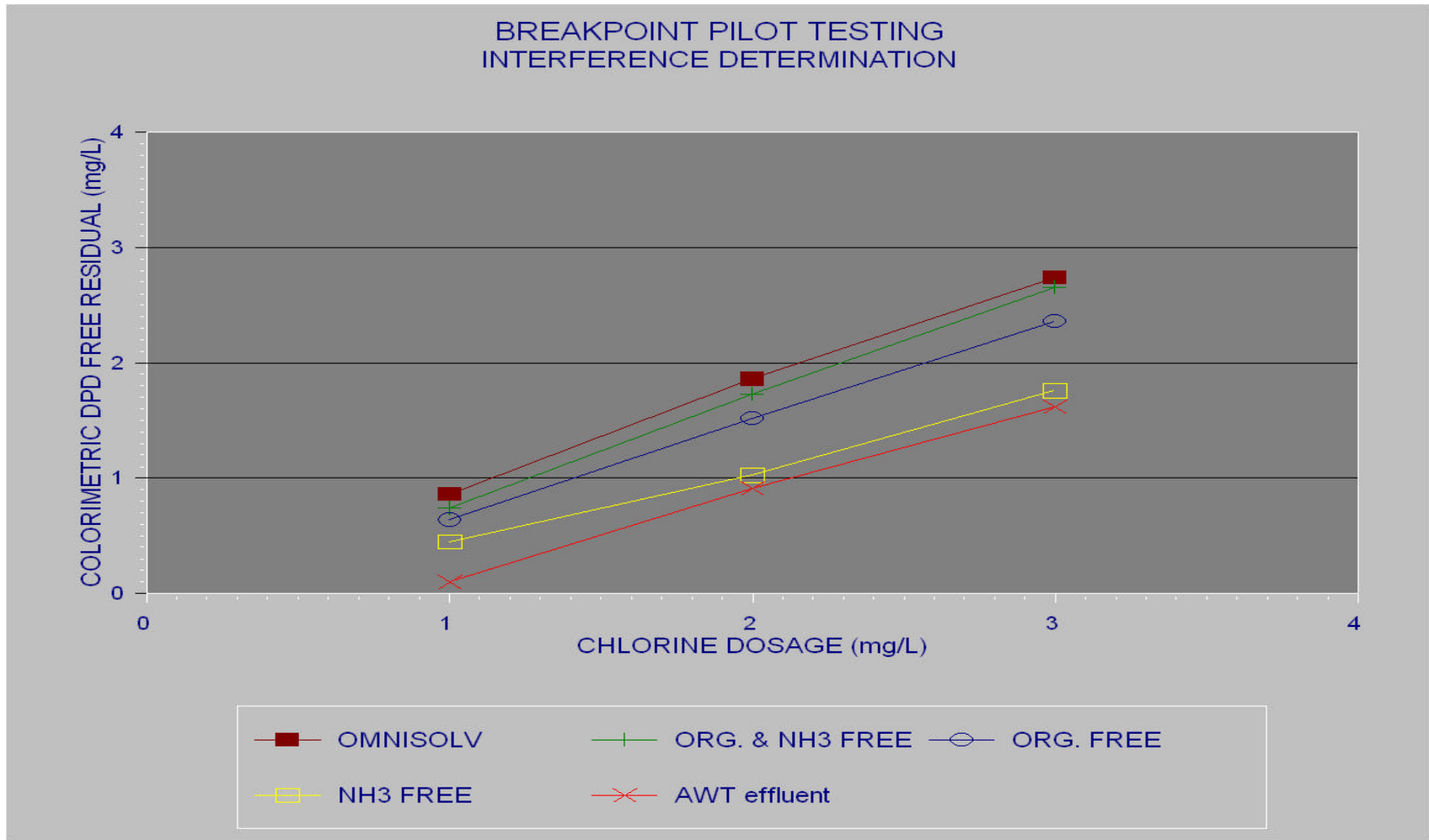


Figure 8. Analysis for Free Chlorine Using DPD Method

Table 3. UOSA Lab Nitrogen Series Analysis Of Waters Used For Interference Study.

<b>UOSA Laboratory - Nitrogen Series Analysis</b>			
(Values are in mg/L)			
<b>Sample</b>	<b>NH<sub>3</sub></b>	<b>TKN</b>	<b>NO<sub>2</sub></b>
*Omni Solv.	<0.02	<0.10	<0.05
AWT Effluent	0.02	0.39	<0.05
AWT Effluent NH3 Free	0.02	0.41	<0.05
AWT Effluent Organic Free	0.03	<0.10	<0.05
AWT Effluent NH3 and Org. Free	<0.02	<0.10	<0.05

< = Below Detection Limit

### **Pilot Study Chlorine Residual Method Comparison**

#### **Cl<sub>2</sub> Speciation**

Two chlorine residual measurement methods were investigated at the pilot plant. Parallel tests were performed using the Amperometric Titration Method (Standard Method 4500-Cl D) and Hach's Titrimetric DPD Method (a modification to Standard Method 4500-Cl F).

#### **Experimental Methods**

In order to compare the two methods of chlorine analysis it was decided to perform parallel testing during pilot operations. This "field testing" provided the opportunity to observe how each test performed under varying breakpoint conditions as well as with numerous operators performing the

tests. Each Test was carried out in accordance with its written procedure, dilutions were made as necessary in order to keep the samples within the range limits of the respective test. Testing was carried out over a period of three weeks and the results are presented in Figure 9.1 and 9.2 and Appendix C.

### **Results and Discussion**

Results show consistently lower free chlorine values for Hach's DPD method than for the amperometric method. The results for total chlorine analysis for the two tests were more in agreement, suggesting an interference in the free measurement. UOSA currently uses amperometric analysis and is most familiar with this test procedure. Although either procedure will provide acceptable results, UOSA operators are more familiar and prefer to use amperometric techniques.

### **Conclusions**

The following conclusions were obtained through the parallel testing.

- 1) The Hach DPD titration method exhibited more variation than the amperometric method especially at residuals greater than 2 mg/L.
- 2) The endpoint of the DPD titration is somewhat subjective and can vary among analysts. The DPD titration endpoint occurs when there is no longer color in the titer. An individual's ability to differentiate between a slight amount of color and no color will affect the result. The endpoint of the amperometric titration occurs when there is no longer a noticeable deflection of an analog indicator and is much more objectively determined. The amperometric titration method is the current chlorine analysis method employed at UOSA and operator familiarity with this method makes it much easier to obtain accuracy and consistency in the results.

- 3) Dilution is required when residuals are greater than 2 mg/L when using the Hach DPD test. The dilution procedure impacts the result in three possible ways:
- a) error in measuring volumes during the dilution procedure,
  - b) dilution requires additional time before titration which allows the reaction to proceed in the titration flask,
  - c) potential for adding chlorine demand in the dilution water (reagent grade water was used for our dilutions).
- 4) Both tests are susceptible to interference's from monochloramine as well as organochloramine in the breakpoint reaction zone. The free residual DPD titration must be performed more rapidly than amperometric titration to eliminate interference's, especially for samples withdrawn from the rapid mix and ten minute contact tanks.

### **Recommendations**

It is recommended that the modified Amperometric Titration Method be used at UOSA to analyze samples for chlorine residuals while the breakpoint chlorination process is operated.

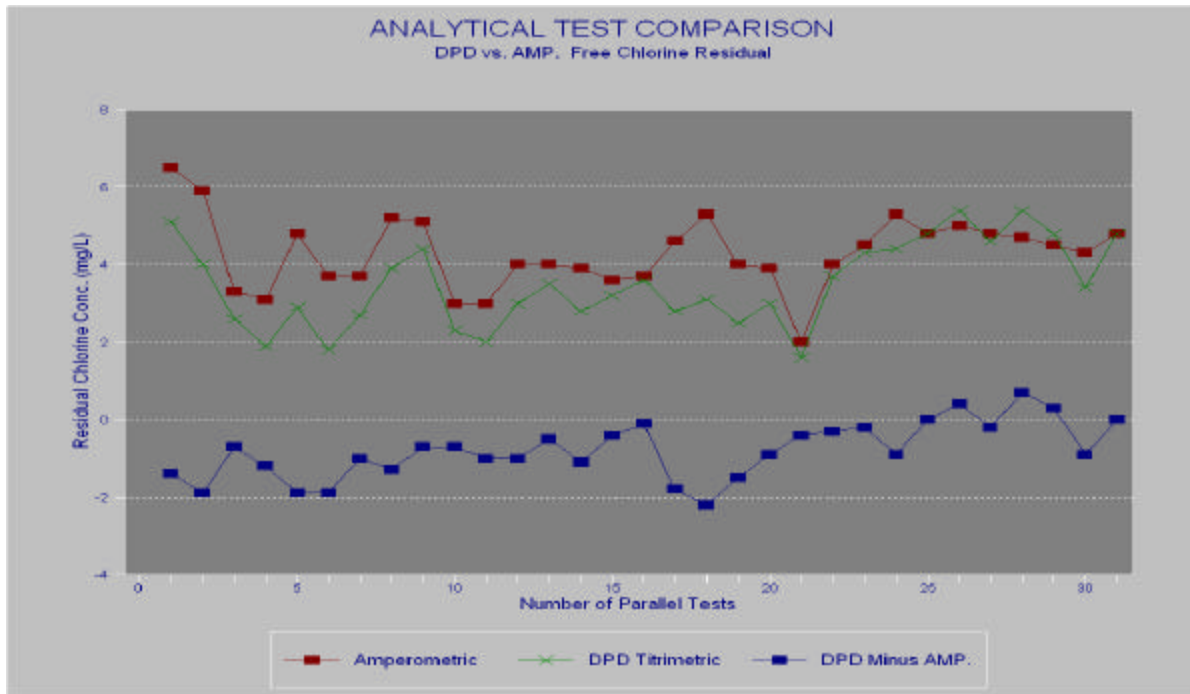


Figure 9.1 DPD vs. Amperometric Analysis for Free Chlorine

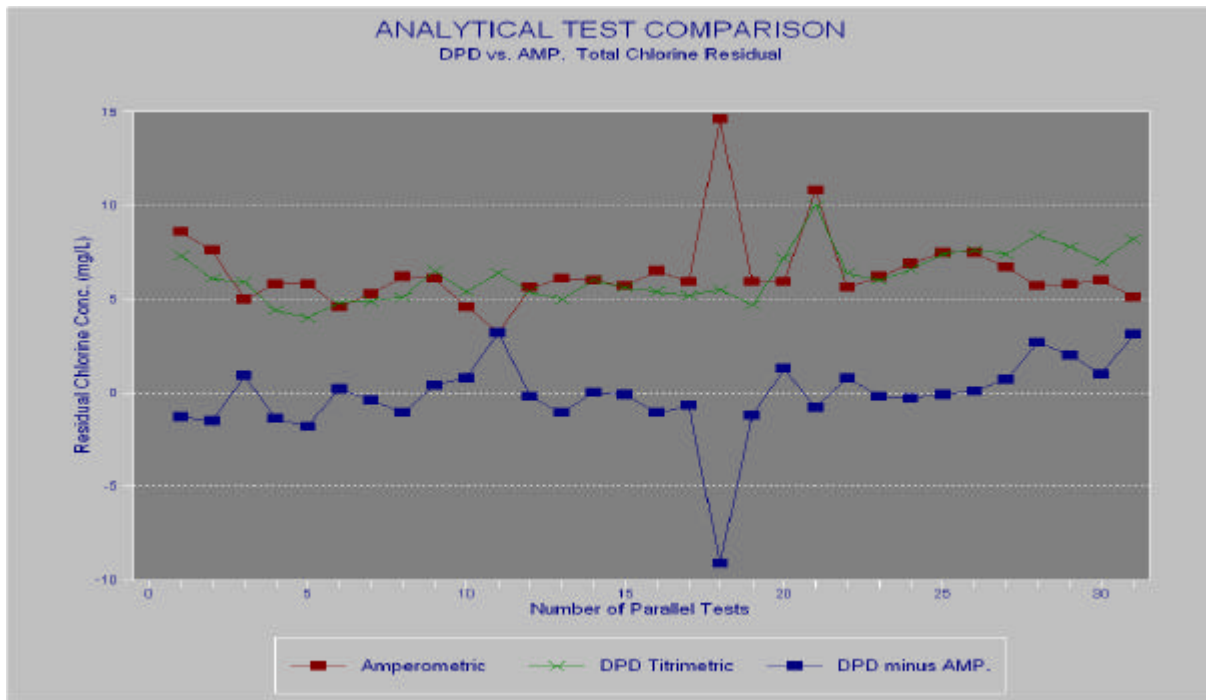


Figure 9.2 DPD vs. Amperometric Analysis for Total Chlorine

## Nitrogen Trichloride (NCl<sub>3</sub>) Analysis

A major objective of the pilot study was to address safety issues for full scale breakpoint operation. One safety concern has been the generation of the highly explosive and toxic gas, nitrogen trichloride.

### Approach

Physical - chemical conditions which promote the formation of NCl<sub>3</sub> during breakpoint are: 1) low initial system pH and 2) Cl<sub>2</sub> : NH<sub>3</sub> dose ratios above 10 - 12:1. Under normal breakpoint pilot operations these conditions are not satisfied and hence, there may not be enough NCl<sub>3</sub> present in the system to measure. In light of these circumstances a special reactor tank (see Figure 10) was used to create conditions which favor the formation of NCl<sub>3</sub>. Since NCl<sub>3</sub> is mostly insoluble in water, and it readily volatilizes under turbulent conditions, it is very difficult to detect the compound in that medium. Since no calibration standards are available for NCl<sub>3</sub> it is also difficult to measure quantitatively. However, the literature suggested a means of qualitative and quantitative analysis of nitrogen trichloride by means of sample extraction with carbon tetrachloride (CCl<sub>4</sub>) followed by sample analysis using UV scanning spectrophotometry (9). The NCl<sub>3</sub> was extracted from the head space of the reactor tank via a PYREX<sup>®</sup> gas washing bottle filled with a known volume of spectrophotometric grade CCl<sub>4</sub>. Once extracted into the CCl<sub>4</sub>, nitrogen trichloride is in a soluble form and can be measured with a U.V. spectrophotometer, with a fingerprint of primary and secondary peaks at 265 & 345 nm respectively. The literature also suggests that quantitative results can be obtained through a ratio determination of primary and secondary peak absorbance (9).



## Experimental Methods

1. The pilot reactor was set up using the existing final effluent tank at the pilot study. This provided the mixer and access ports needed to conduct the experiment. The tank was sealed with duct tape and removable rubber stoppers to provide access to add chemicals. A sampling port was provided for a grab analysis to assure operating guidelines (pH, initial ammonia concentration and  $\text{Cl}_2:\text{NH}_3$  dose ratio) were met.

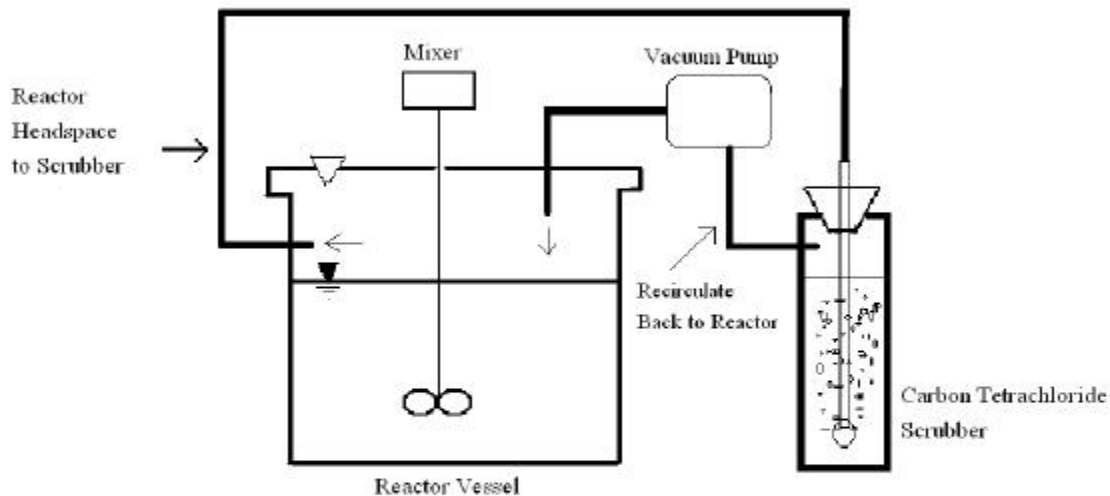


Figure 10. NCl<sub>3</sub> Static Test Reactor

2. The water in the reactor tank (Fig.10) was UOSA final filter effluent of a known volume. A pre-determined mass of ammonium chloride ( $\text{NH}_4\text{Cl}$ ) was added resulting in a final ammonia concentration of  $\sim 11.0$  mg/L  $\text{NH}_3\text{-N}$ . Diluted sulfuric acid was added for pH adjustment. Calculated volumes of 5.25% sodium hypochlorite were added to reach the breakpoint at the varying dose ratios desired.

3. The reaction proceeded in the sealed tank for approximately 24 hours with constant, vigorous mixing. During this time the head space of the tank was pumped, via a 12V DC Cole-Parmer Model #7530-25 diaphragm pump and Tygon® tubing, through a gas scrubber filled with a known volume of  $\text{CCl}_4$ . This allowed any existing  $\text{NCl}_3$  in the system to transfer from the aqueous phase (in water) to the gaseous phase in the head space and finally back to the soluble phase in  $\text{CCl}_4$ . The gas exiting from the scrubber was recirculated back into the reactor for reprocessing through the system. This allowed maximum transfer of any existing  $\text{NCl}_3$  into the  $\text{CCl}_4$ .

4. At the end of the 24 hour period the  $\text{CCl}_4$  was collected and analyzed using a scanning UV spectrophotometer at wavelengths between 200 and 400 nm. The primary and secondary peaks of  $\text{NCl}_3$  in  $\text{CCl}_4$  occur at 265 and 345 nm, respectively.

## **Results and Discussion**

Batch testing was performed over a period of several days using several different  $\text{Cl}_2\text{:NH}_3$  dose ratios and different system pHs. While the results (Figure 11 and Table 4) show an increase in  $\text{NCl}_3$  as the pH decreased and  $\text{Cl}_2\text{:NH}_3$  dose ratio was increased, production of  $\text{NCl}_3$  appears to be more dependant on low system pHs ( $<6.0$ ) than higher dose ratios ( $>10:1$ ). The most severe  $\text{NCl}_3$

formation appears when operating with both low system pH and a high  $\text{Cl}_2:\text{NH}_3$  dose rate. Operational data can be found in Appendix D.

UOSA currently uses NaOCl for disinfection and will use it for Breakpoint operations, low pH levels are not a major concern. It is however, recommended that NaOH feed be available for situations where high ammonia concentrations are encountered, to avoid any possibility of  $\text{NCl}_3$  generation.

### **Conclusions**

Based on results from the batch testing it is recommended that the breakpoint facility be operated at a high pH ( $>7.0$  after 30 minutes detention) and low initial  $\text{Cl}_2:\text{NH}_3$  dose ratios ( $<10.0$ , depending on influent water quality) to prevent the formation of high concentrations of  $\text{NCl}_3$ .

### **Ammonia Nitrogen Analysis**

Two ammonia measurement methods were investigated at the pilot plant. Parallel tests were performed using the Phenate Method (Standard Method 4500-NH<sub>3</sub> D) and the Ammonia Selective Electrode Method (Standard Method 4500-NH<sub>3</sub> E).

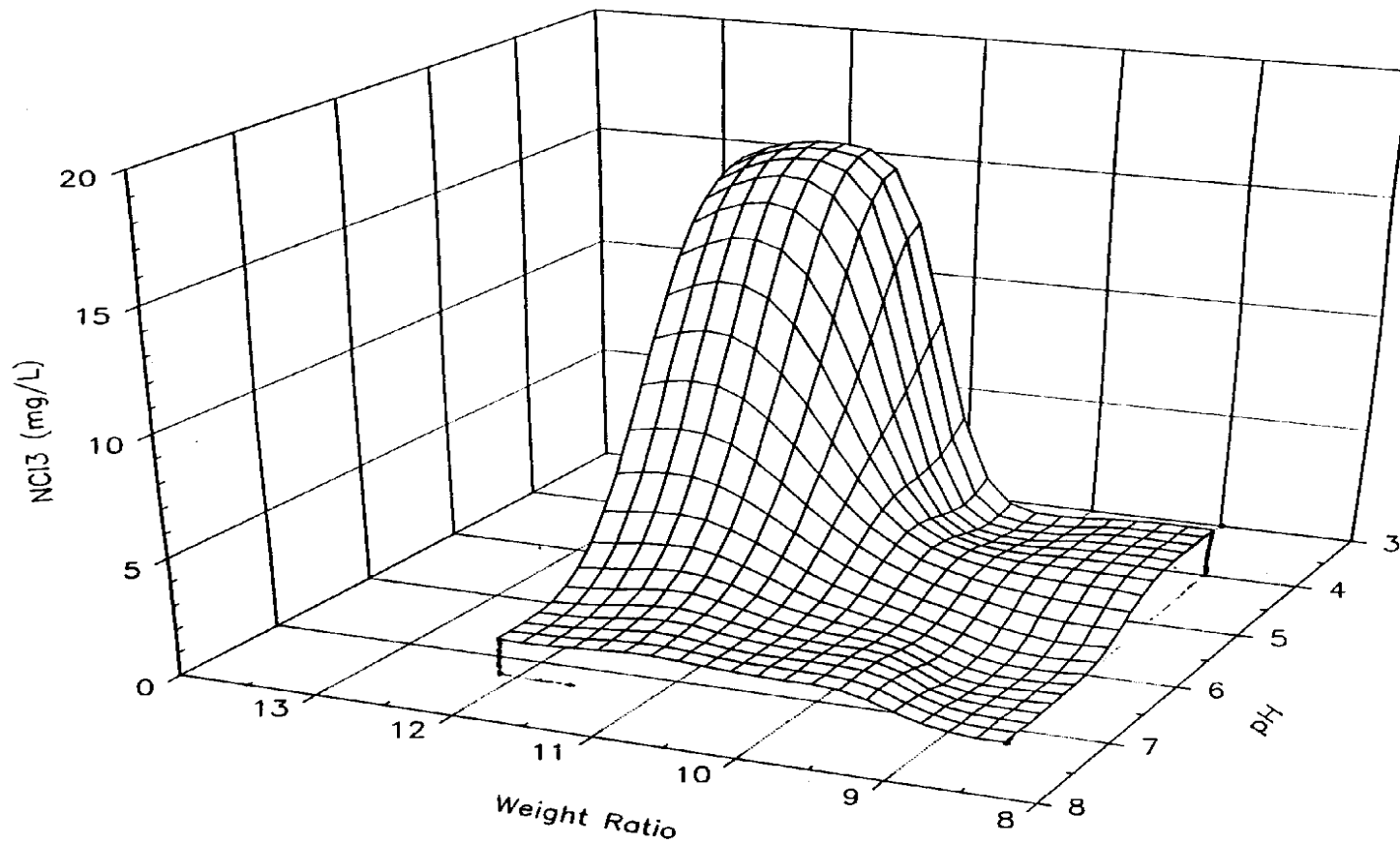


Figure 11. Plot of  $\text{NCl}_3$  Data from Reactor Studies

Table 4. Data from UV Analysis of Samples from NCl<sub>3</sub> Reactor

<b>Special Study of Nitrogen Trichloride</b>		
<b>Cl<sub>2</sub>:NH<sub>3</sub> Weight Ratio</b>	<b>Final Reactor pH</b>	<b>Estimated NCl<sub>3</sub> (mg/L)</b>
(Data below are from lower pH runs)		
11.5:1	4.1	17
9.8:1	4.4	2
9.0:1	4.5	2.3
(Data below are from higher pH runs)		
12.2:1	7.2	1.3
10:1	6.8	1.3
9:1	6.4	*ND
8.6:1	7.0	*ND

\*ND = Not Detected

### **Discussion**

The following conclusions were obtained through the parallel testing.

- 1) Significant positive interference from chloramines occurs when using the phenate method for samples taken in the early stages of breakpoint chlorination. The phenate method yielded positive ammonia results in the presence of free and combined chlorine residual. Ammonia results using the phenate method were not reliable, accurate, or precise in the presence of high concentrations of chloramines. This was especially true when samples from the rapid mix or contact tanks are analyzed.
- 2) The ion selective electrode method required special precautions to generate reliable, precise, and accurate results. These include checking calibration once per shift for drift, recalibrating at least daily with fresh standards, and membrane replacement at least weekly.

### **Recommendations**

The Ammonia Ion Selective Method is recommended for analysis of breakpoint chlorination samples.

### **Breakpoint Characterizations**

Special tests were conducted to re-create the breakpoint curve under varying chlorine to ammonia dose ratios (5:1, 8:1, 10:1, and 12:1) at rapid mix pHs 7.0, 7.5, 8.0, and 8.5.

### **Experimental Methods**

The initial ammonia concentration for the pilot was adjusted to 11.0 mg/L and was monitored throughout the study. Chlorine dosages were calculated based on initial chlorine tank concentration (mg/L), transfer pump speed (ml/min), and pilot plant flow (gpm). The pilot plant flow for this study was adjusted to 2.4 gpm in order to obtain a 45 minute total detention time for the study. pH adjustment was done with sodium hydroxide in order to achieve the desired rapid mix tank pH at a dose ratio of 8:1 (chlorine to ammonia). After the initial adjustment, at an 8:1 dose rate, the sodium hydroxide feed rate remained the same for all dose ratios used throughout that particular pH run. Steady state conditions were achieved before any testing was initiated.

### **Results and Discussions**

Testing was done over a four day period and the results of the 30 minute contact data are presented in Figures 12-15, and also in Appendix E. As is indicated from these 30 minute curves, monochloramine presence decreases at weight ratios less than the breakpoint as the pH increases from 7.0 to 8.0 then increases again at pH 8.5. There was also a noticeable decrease in the amount of total chlorine remaining at the breakpoint (8:1 dose ratio) as the pH increased from 7.0 to 8.5. At higher chlorine dose ratios the amount of combined chlorine residual present after breakpoint, as a fraction of total chlorine, decreased as the pH increased from 7.0 to 8.0 then increased again at pH

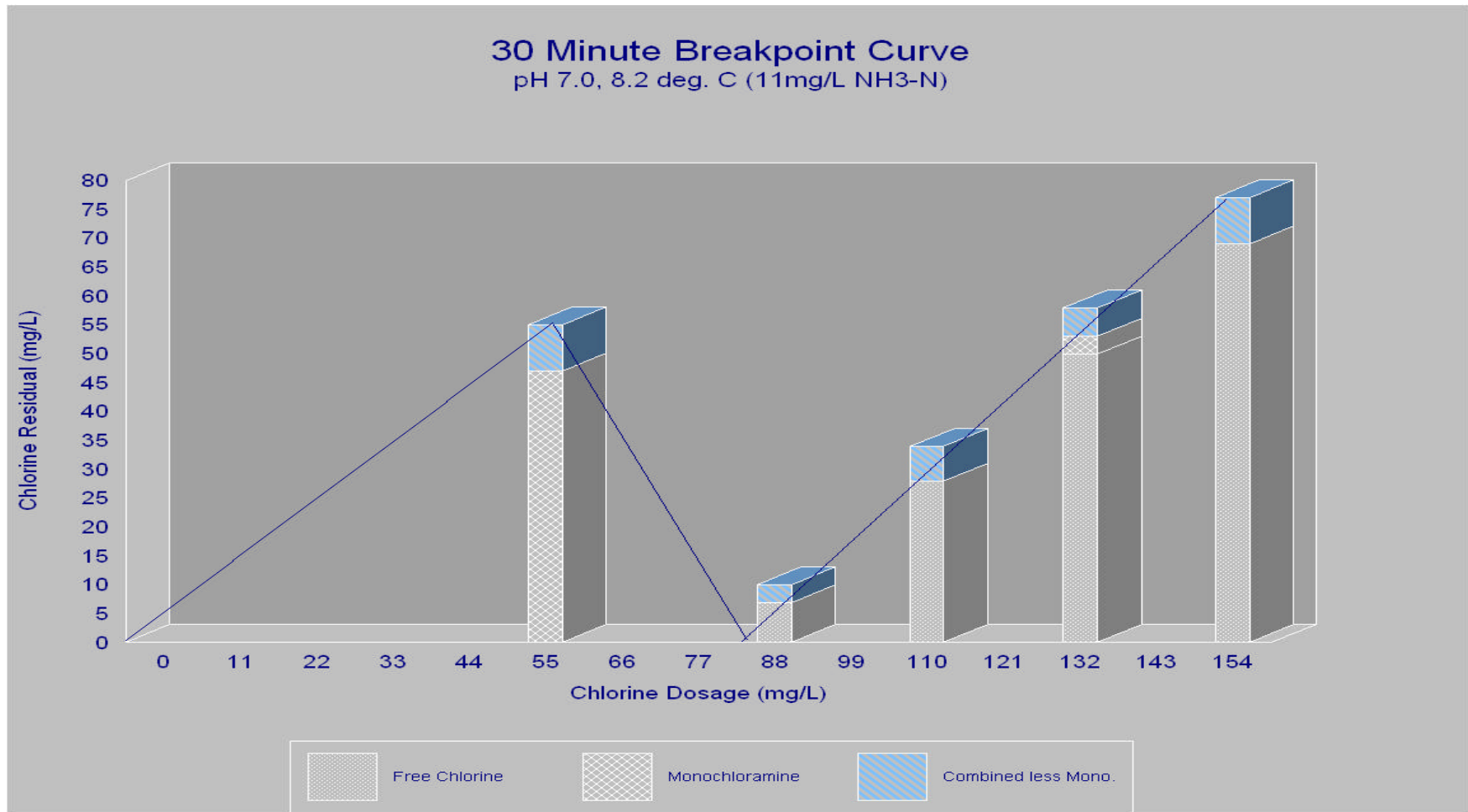


Figure 12. Breakpoint Characterizations pH = 7.0,(x axis scaled to correspond with 11 mg/L NH<sub>3</sub> Dosage)

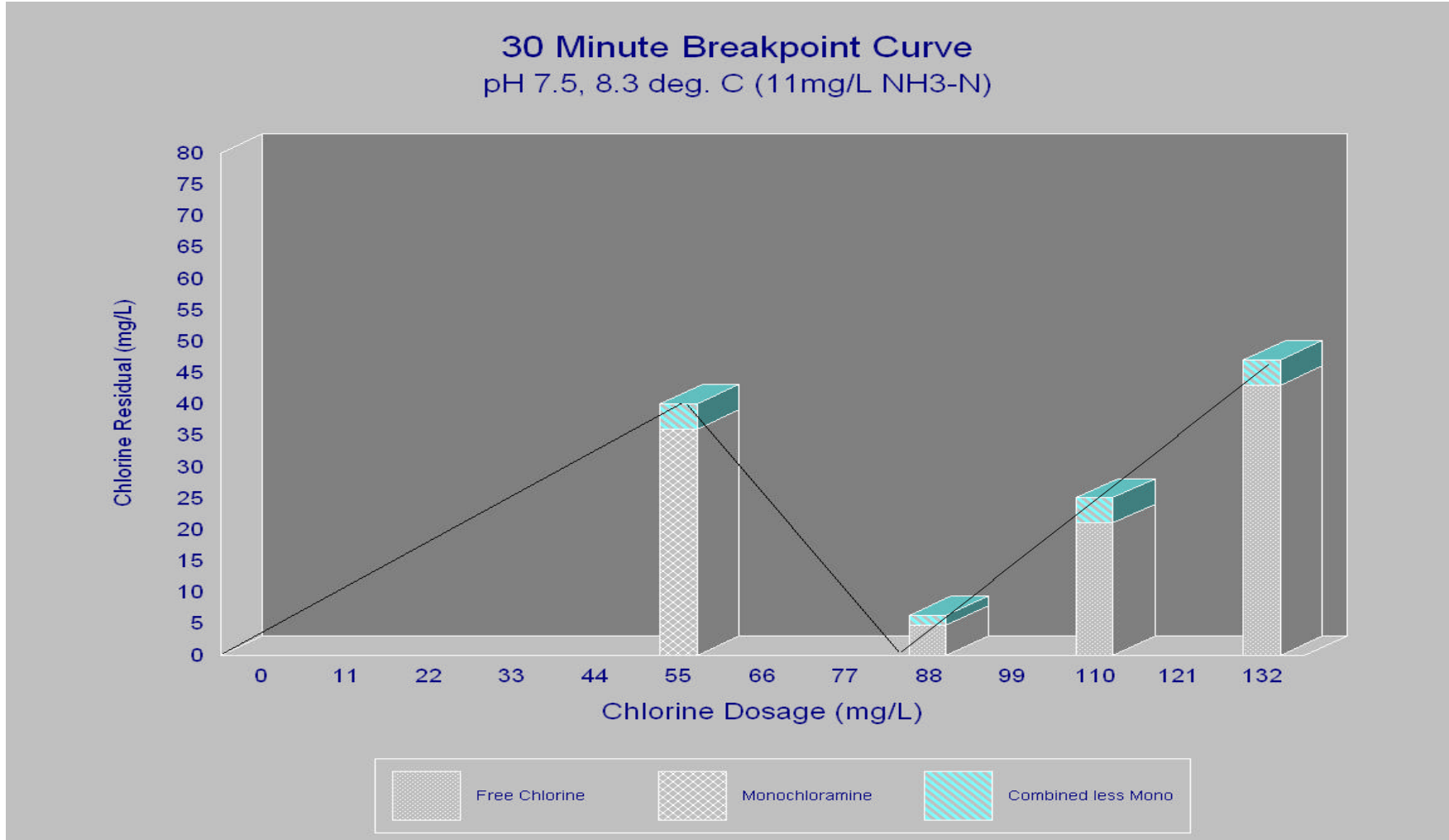


Figure 13. Breakpoint Characterizations pH = 7.5,(x axis scaled to correspond with 11 mg/L NH<sub>3</sub> Dosage)



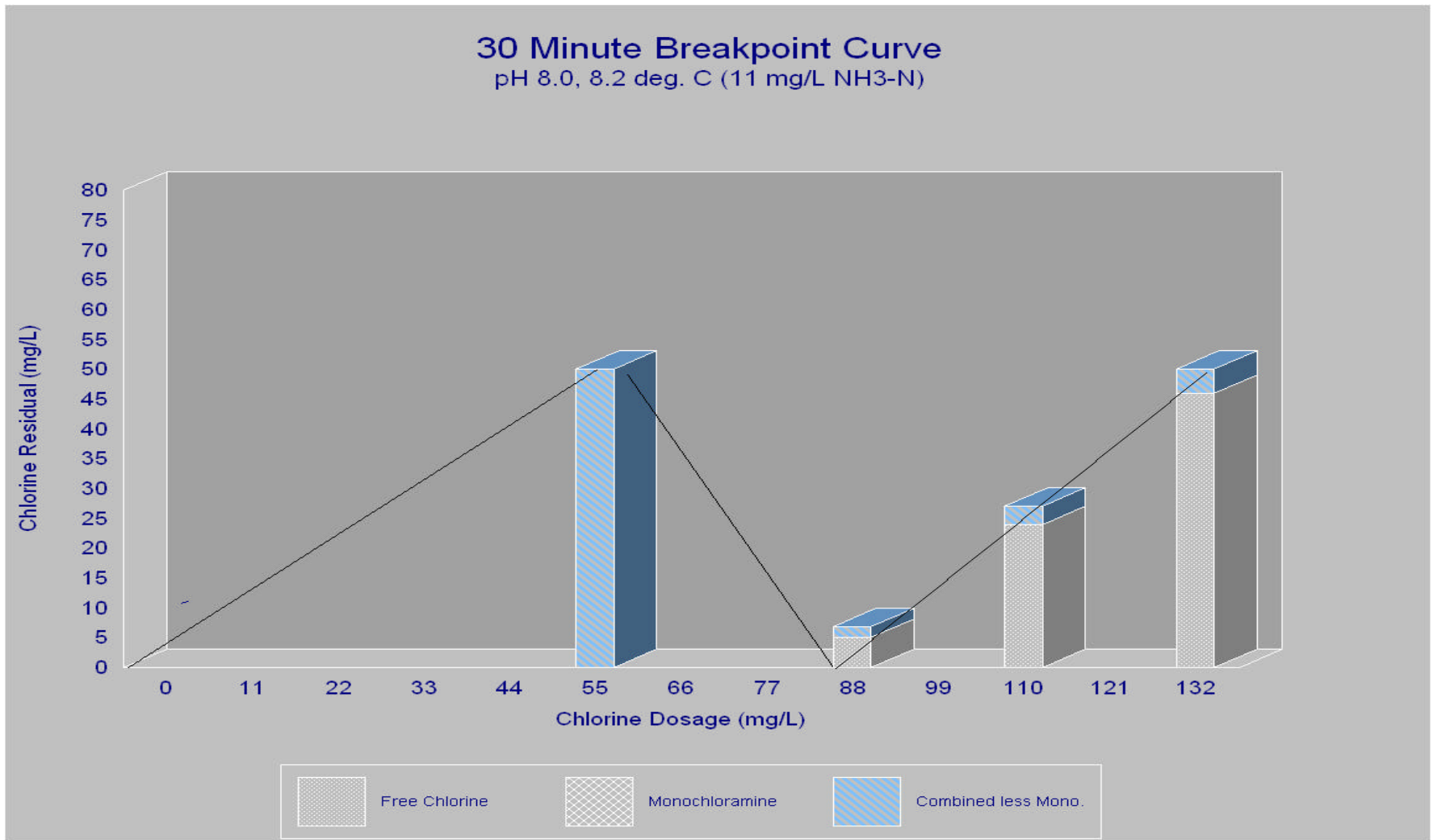


Figure 14. Breakpoint Characterizations pH = 8.0,(x axis scaled to correspond with 11 mg/L NH<sub>3</sub> Dosage)

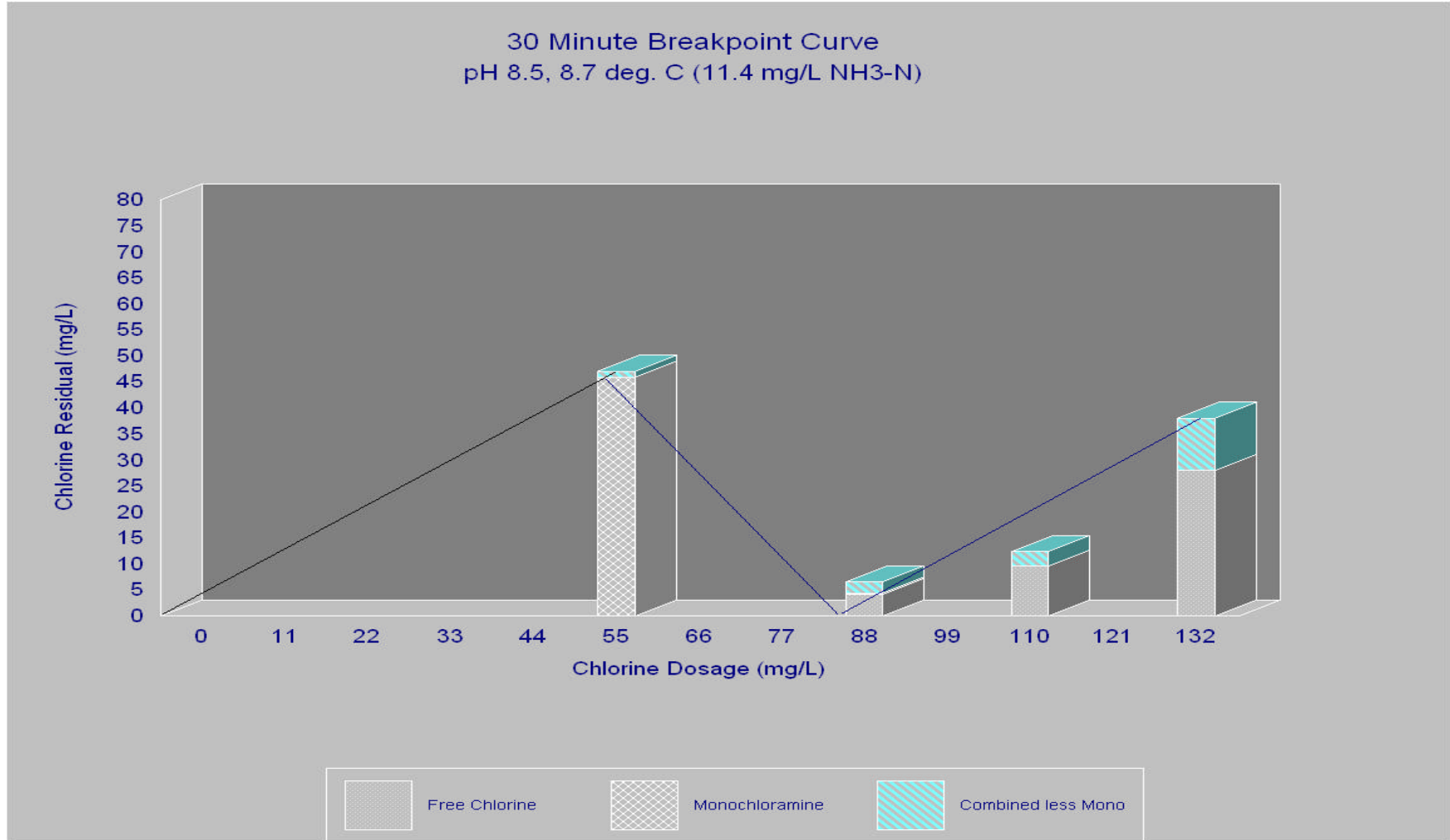


Figure 15. Breakpoint Characterizations pH = 8.5,(x axis scaled to correspond with 11 mg/L NH<sub>3</sub> Dosage)

8.5. The appearance of high concentrations of dichloramine before breakpoint at pH 8.0 was entirely unexpected, and is suspect. However, based on the large number of analysis taken and the exact duplication of the testing protocols throughout this study the data was considered reliable. (Appendix E). Further testing of this occurrence was not possible due to the time consuming nature of these characterizations and associated funding constraints. Dechlorination and subsequent ammonia analysis during the characterizations (see Appendix E) revealed that the best ammonia removal occurred at an 8:1 Cl<sub>2</sub>: NH<sub>3</sub> weight ratio for all pHs tested. As the weight ratio increased beyond 8:1 the residual ammonia concentration increased. As pH increased from 7.0 to 8.5 the amount of residual ammonia after dechlorination decreased. It was noted that at pH 7.0 and 8.5 there was free ammonia present (before dechlorination) at 5:1 dose ratios before breakpoint.

### **Conclusions**

The Breakpoint reaction performs best at pHs of 7.5 to 8.0, at a dose ratio (Cl<sub>2</sub>:NH<sub>3</sub>) as close to stoichiometric (7.6:1) as possible.

## *Materials and Methods*

### **Pilot Plant Description**

A schematic of the pilot plant is presented in Figure 16. The pilot plant was a continuous flow design with a flow rate of 3.4 gpm. UOSA Advanced Waste Treatment (AWT) effluent was used as the feed water source for the pilot plant, and because of its high quality had to be spiked with  $\text{NH}_3\text{-N}$ . The pilot plant consisted of a series of continuously stirred tank reactors (CSTRs), with the exception of the head tank and wet well. Effective detention times for all pilot tanks and the system as a whole were determined by the dye study previously described. UOSA AWT effluent was fed to a recirculation tank. Flow into this tank was controlled with a float switch to maintain a constant volume of 50 gallons. An APEC chiller was used to lower the influent water temperature to approximately 8 °C (UOSA worst case temperature conditions). Chemicals used for the pilot study were batched as needed in 50 and 100 liter cylindrical Nalgene™ tanks using UOSA laboratory deionized water (prefiltered water, processed through both carbon and ion exchange media's). All chemicals used in the pilot study were fed via Masterflex L/S™ variable speed peristaltic pumps, with a 10:1 turn down. Pump speeds, pump heads, and tubing sizes were varied to achieve the desired influent concentration of the specific reagent. Masterflex C-Flex™ pump tubing was used specifically in all peristaltic pump heads, all tubing leading to and from the pump head tubing was

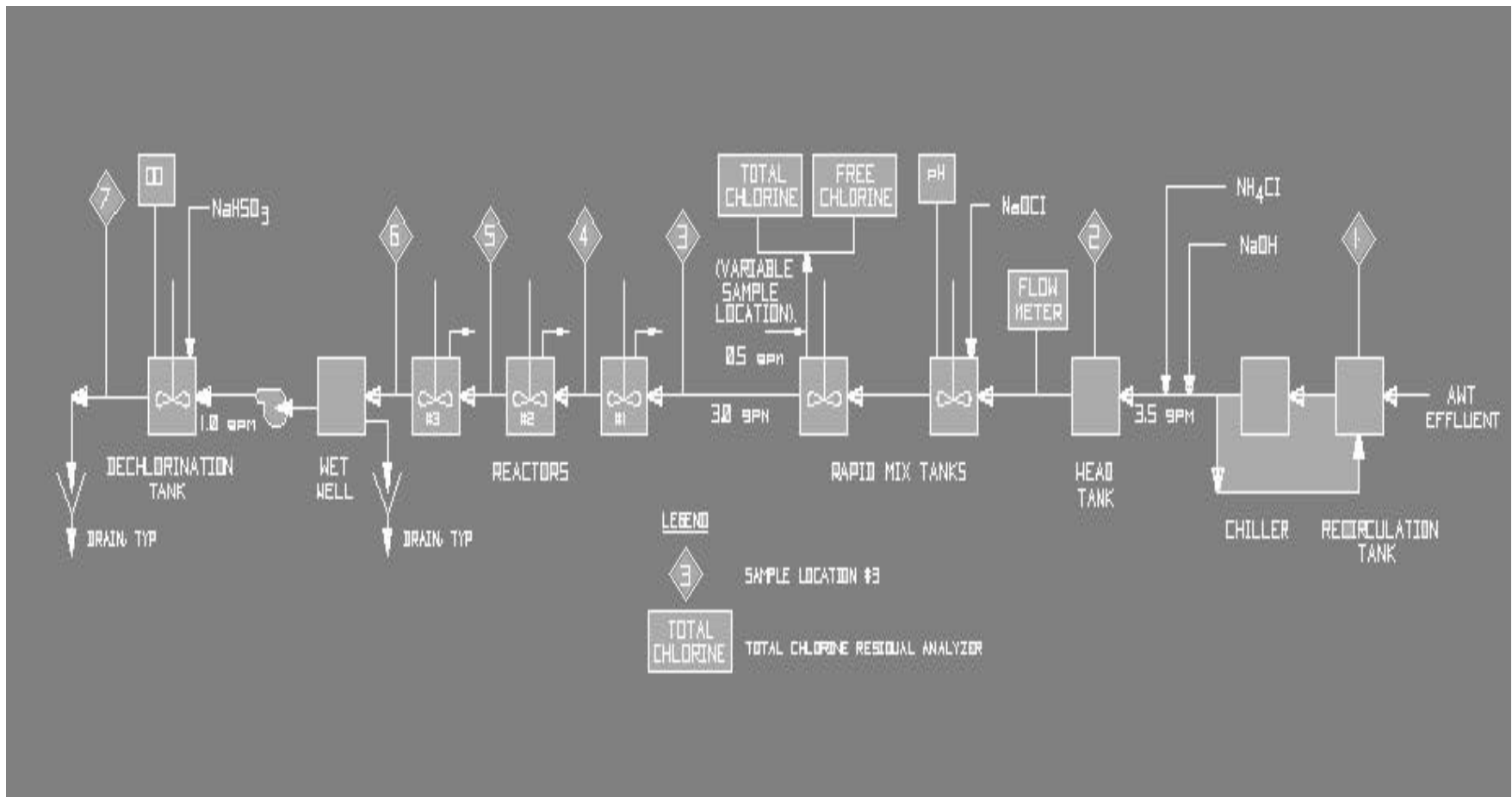


Figure 16. Breakpoint Pilot Plant Schematic

Masterflex Norprene<sup>TM</sup>. Pilot reactor tanks were square, polyethylene tanks with the following volumes: head tank and effluent wet well volume = 7.8 gallons, rapid mix tank volumes = 4.3 gallons, and contact tank 1, 2, and 3 volumes = 33.7 gallons each. All tanks were connected with PVC piping and union couplings. Each tank in the system was connected to a centralized off-gas removal system. This system, which operated under a low negative pressure, was designed to remove any gasses accumulating within the head space of the pilot plant tanks. The off-gas collection system was constructed with PVC piping, flexible plastic hoses, and a 1725 rpm explosion proof exhaust blower. Exhaust gasses were directed to the outside of the building. Mixers for the CSTRs were a variable speed type for the smaller tanks and dual speed for the larger contact tanks. Water was transferred from the effluent wet well of the pilot with a large Masterflex peristaltic pump to a dechlorination tank. All pilot plant effluent was directed to the plant waste pump station for treatment through the UOSA wastewater reclamation plant.

### **pH control**

Pilot operation at pH 7.5 and 8.0 required addition of sodium hydroxide solution to reach and maintain the setpoint pH within the rapid mix tank. This solution was prepared using reagent grade sodium hydroxide pellets dissolved in a large Nalgene<sup>TM</sup> cylindrical tank. The working concentrations of hydroxide were ~ 0.1 M for the pH 7.5 run and ~0.5 M for the pH 8.0 run. This solution was injected into the pilot flow before the pilot head tank.

### **Ammonia Feed**

Ammonia was added to the pilot in the form of ammonium chloride (NH<sub>4</sub>-Cl) solution in order to obtain the desired initial ammonia concentration (as NH<sub>3</sub>-N) in the head tank. Reagent grade NH<sub>4</sub>-Cl

was used and the solution strength was ~0.34 M. The  $\text{NH}_4\text{-Cl}$  solution was injected into the pilot flow before the pilot head tank. Pilot influent  $\text{NH}_3\text{-N}$  feed was periodically monitored by sampling the water in the head tank. The head tank samples were analyzed for  $\text{NH}_3\text{-N}$  with an Ion Specific Electrode (ISE) and the  $\text{NH}_4\text{Cl}$  feed pump was subsequently adjusted to maintain the desired  $\text{NH}_3\text{-N}$  in the pilot rapid mix tank.

### **Chlorine Feed**

A 12-15% solution of sodium hypochlorite was purchased in 55 gallon barrels for the study. The concentration of the solution was determined amperometrically (after sample dilution) upon opening of a new barrel and periodically while in use because of the potential for feedstock decay and destabilization. The average strength of the hypochlorite was ~12.5-13.5%. This solution was injected at the breakpoint rapid mix tank just below the mixing blade. Feed rate was determined by process performance.  $\text{Cl}_2$  dosage and  $\text{Cl}_2\text{:NH}_3$  weight ratios were calculated based on feedstock concentration, feed rate as a percent of maximum pump capacity and pilot flow rate.

### **Sodium Bisulfite**

Dechlorination was performed using a sodium bisulfite/sodium metabisulfite solution. The reagent grade dry chemical was mixed with water in a 50 liter cylindrical Nalgene™ tank. The concentration was ~0.04 M as  $\text{SO}_2$  and was injected into the dechlorination tank. The feed rate was adjusted so that a non-detectable chlorine residual resulted upon analysis of a pilot plant effluent sample.

### **Pilot Plant Phase I Design Criteria**

Influent NH <sub>3</sub> -N	-	11.0 mg/L
Rapid Mix pHs	-	7.0, 7.5, 8.0
Pilot Flow	-	3.4 gpm
Influent Alkalinity	-	~100 mg/L as CaCO <sub>3</sub>
Influent Cl <sub>2</sub> Dose (Cl <sub>2</sub> :NH <sub>3</sub> -N Dose Ratio = 8:1)	-	~88 mg/L
HDT	-	~30 mins.
Temperature	-	~8 °C

### **Pilot Plant Phase II Design Criteria**

Influent NH <sub>3</sub> -N	-	2.0 & 6.0 mg/L
Influent Org-N	-	~1.0 mg/L
Influent NO <sub>2</sub> -N	-	~5.0 mg/L
Pilot Temperature	-	12 & 20 °C
Rapid Mix pH	-	8.0
Pilot Flow	-	~3.2 gpm
Influent Cl <sub>2</sub> Dose (Cl <sub>2</sub> : NH <sub>3</sub> Dose Ratio = 8:1)	-	~88 mg/L
HDT	-	30 mins.



## **Pilot Plant Operation**

Phase I pilot operations were performed in three sub-phases, IA, IB, and IC. Each sub-phase corresponded to breakpoint operations at pH values of 7.0, 7.5, and 8.0 respectively. During operation, the pilot plant was manned at all times. Breakpoint operations were shut down between each pH phase of the pilot study in order to assemble, compile, and review all data generated during that particular pH run. Phase II pilot operations were performed using the optimum setpoints (pH, chlorine dose, detention time) as determined from Phase I operation.

## **Duration**

Each Phase I sub-phase was operated at steady state for four weeks to provide enough data to be statistically relevant. This time was divided into three weeks of eight hour a day, 5 day a week monitoring and one week of 24 hour a day, 7 day a week monitoring. The 24 hour monitoring was incorporated into each phase of the steady state operation to determine if any diurnal or weekly variations in influent water quality would be significant. Although the pilot plant was operated for 24 hours a day during the 3 week, 5 day a week period; operator staffing limited monitoring to an 8 hour period each day. The pilot plant was not operated on weekends during this period to reduce chemical usage. Phase II testing consisted of pilot operation 8 hours a day, 5 days a week. The pilot was shut down during the off hours, with the exception of the flow and a slight chlorine feed to prevent fouling of the reaction tanks or calibration drift of the instrumentation.

## **Pilot Plant Instrumentation**

### **On-Line Field Instruments**

On-line instrumentation was used to constantly monitor the operation of the pilot plant. During operation of the pilot different instrumentation from manufacturers of on-line instrumentation were tested for reliability and accuracy under varying breakpoint operating conditions.

#### **On-line Cl<sub>2</sub> Analyzers**

Two different manufacturers of on-line chlorine analyzers were used at the pilot plant:

Capital Controls Series 1870E Free and Total Chlorine Analyzers were installed at the start of the pilot study and remained throughout the duration of the three year pilot operation.

A Wallace & Tiernan Micro/2000<sup>®</sup> Free Chlorine Analyzer was installed during the last few weeks of operation in order to evaluate the differences (see Phase II) in the two instruments.

#### **On-Line NH<sub>3</sub> Analyzers**

Instrumentation from two different manufacturers of on-line ammonia analyzers were tested at the pilot plant:

A PHOX model 1801 Mk2 on-line ammonia analyzer was tested at the pilot study. This unit was based on Ion Specific Electrode technology.

A TYTRONICS model FPA 800 on-line ammonia analyzer was tested during the last few weeks of pilot operation. This unit was based on colorimetric (Nessler reagent) technology.

### **On-Line pH Monitoring**

The pH of the pilot plant was monitored in rapid mix tank #1 and provided a quick and accurate means of monitoring the pH of the breakpoint reaction. A TBI model 515 on-line pH meter was initially used in the pilot plant, this was damaged by an electrical surge and subsequently replaced with a FOXBORO model 871 on-line pH meter.

### **On-Line Dissolved Oxygen Meter**

A CAPITOL CONTROLS model 1865 on-line D.O. meter was used in the pilot plant. This was a membrane and electrolytic cell type instrument.

### **Pilot Flow**

A SIGNET model 586 flow meter was used in the pilot plant but was replaced with a SIGNET model 90110 during the last few months of operation.

## **Analytical Methods**

### **Pilot Plant Methods**

#### **QA/QC**

Field sample analysis was subject to random repeat analysis in order to insure that pilot analysis was meeting quality control guidelines for precision. Initial and infrequent analysis of prepared chlorine standards were performed to identify accuracy of the test methods. However, routine spikes to determine accuracy and % recoveries were not performed because of the already taxing analytical schedule for field testing.

#### **Chlorine Species**

Free and combined chlorine species measurements were made using a Wallace and Tiernan Amperometric Titrator series A 790 with a +200 mv applied potential to the platinum electrode. The procedure was a slight modification to Standard Methods 4500-Cl D.

#### **Ammonia Nitrogen**

Ammonia analysis was done with a Fisher Accumet 25 Ion Selective Electrode Meter. This meter was used in conjunction with an Orion 9512BN Ammonia Ion Selective Electrode. The pilot procedure for ammonia analysis was in accordance with Standard Methods 4500-NH<sub>3</sub>F. A two point calibration curve was performed with fresh ammonia standards every morning and standard curves

were updated periodically during the day. Due to the "clean" nature of the water used for the pilot study, it was not necessary to replace the electrode membrane as often as was expected.

### **Nitrite Nitrogen**

Field analysis of Nitrite Nitrogen was performed with a HACH test kit for Nitrite. Samples were analyzed with a Bausch and Lomb Spec 20 at 585 nm according to HACH instructions. A standard curve was prepared daily with fresh NO<sub>2</sub>-N standards.

### **pH**

pH was measured with an Orion model 250A portable pH meter and accompanying Triode Combination Electrode/ATC probe. Calibration was done daily with purchased certified buffers.

### **Alkalinity**

Total alkalinity was determined with a Hach Digital titrator and accompanying 0.1600 N sulfuric acid cartridges. The test was done to the pH end point of 4.5.

### **Dissolved Oxygen**

D.O. was determined with a YSI model 51B portable D.O. meter. Air calibration was performed daily and membrane replacement and probe service was performed when needed.

### **Temperature**

Temperatures profiles were initially performed using the Orion pH triode, and later in the study with the YSI D.O. probe. Both units have built in temperature probes.

## **UOSA Laboratory Methods**

### **QA/QC**

Laboratory data for all analysis performed by the UOSA laboratory was subject to, and passed, an in house QA/QC program for accuracy and precision.

### **Ammonia, Nitrite, Nitrate**

Laboratory analysis of ammonia, nitrite, and nitrate was performed with a Technicon trAAcs™ 800 colorimetric low level Auto Analyzer, in accordance with their methods for industrial analysis.

### **TKN**

TKN was analyzed on a Technicon colorimetric Auto Analyzer II, after sample digestion and preparation, according to EPA Method 351.2.

## **COD**

COD (Chemical Oxygen Demand) was measured colorimetrically with USEPA approved Hach closed reflux micro method.

## **TSS/TS**

Total suspended solids and total solids measurement were performed in accordance with standard methods 2540 D. and 2540 B. respectively.

## **Fecal Coliforms**

Fecal Coliforms were determined using the membrane filter technique and analysts followed Standard Method 9230 C. procedures.

## **Contracted Laboratory Methods**

### **QA/QC**

All contracted laboratory data passed QA/QC guidelines set forth by the respective outside laboratory performing the analysis. There were no exceptions.

**Purgeable Halocarbons / Aromatics** were determined using EPA methods 601/602 respectively.

**Total Organic Halogens** were determined using EPA method 9020.

**Chlorinated Disinfection Byproducts / Haloacetic Acids** were determined using EPA method 551/552 respectively.

## Analytical Monitoring Program

The analytical monitoring program for Phase I is shown in Table 5. The analytical monitoring program for Phase II is shown in Tables 6 and 7. These indicate the sampling points, sampling frequency, the type of sample (grab or composite), the analysis, and the proposed laboratory location for the analytical work.

Table 5. Monitoring Program for Pilot Plant

ANALYTICAL MONITORING – PROGRAM - PHASE I							
PARAMETER	SAMPLE POINTS (see Figure 16)						
	1	2	3	4	5	6	7
FREE CHLORINE			C & 2HG/PP	2HG/PP	2HG/PP	2HG/PP	2HG/PP
TOTAL CHLORINE			C & 2HG/PP	2HG/PP	2HG/PP	2HG/PP	2HG/PP
MONOCHLORAMINE			2DG/PP	2DG/PP	2DG/PP	2DG/PP	2DG/PP
DI-CHLORAMINE			2DG/PP	2DG/PP	2DG/PP	2DG/PP	2DG/PP
AMMONIA	DC/UOSA	2HG/PP & DC/UOSA	2DG/PP	2DG/PP	2DG/PP	2HG/PP & DC/ UOSA	2HG/PP & DC/UOSA
TKN	DC/UOSA	DC/UOSA					DC/UOSA
NITRITE	DC/UOSA	DC/UOSA					DC/UOSA
NITRATE	DC/UOSA	DC/UOSA					DC/UOSA
DBP		WG/OL					WG/OL
PH		2HG/PP	C & 2HG (1)	2HG/PP	2HG/PP	2HG/PP	DG/PP & C (1)
ALKALINITY		DG/PP					DG/PP
DISSOLVED O <sub>2</sub>		DG/PP					DG/PP & C (1)
TEMPERATURE	2DG/PP	2DG/PP					2DG/PP
COD	DC/UOSA	DC/UOSA					DC/UOSA
TSS	DC/UOSA	DC/UOSA					DC/UOSA
MERCURY	DC/UOSA						WC/UOSA
FECAL COLIFORM							WG/UOSA

### Legend

C	Continuously Monitored	WG	Weekly Grab Sample
G	Grab Sample	DC	Daily Composite
DG	Daily Grab Sample	WC	Weekly Composite
HG	Hourly Grab Sample	PP	Pilot Plant Lab
2DG	Grab Sample Twice Daily	UOSA	UOSA Plant Lab
2HG	Grab Sample Every Two Hours	OL	Outside Lab

(1) See Figure 16 For Exact Sample Location



### UOSA Laboratory Analysis

The UOSA laboratory staff were responsible for analyzing two composite samples per day for the pilot operation. Samples were collected at the influent and effluent of the pilot plant by the pilot plant engineer.

Table 6 - *Laboratory Analytical Monitoring Program*

Test Scenario	Laboratory Analysis Performed					
	NH <sub>3</sub> -N	TKN	NO <sub>2</sub> -N	COD	TSS	* Disinfection By-Products
Variable Temperature	X	X				
Variable Ammonia (NH <sub>3</sub> -N)	X	X				
Increased Organic Nitrogen	X	X		X	X	X
Increased Nitrite Nitrogen	X	X	X			

\* = Grab sample, sent to outside laboratory for analysis.

### Pilot Plant Analysis

The Pilot Plant engineer was responsible for analyzing grab samples twice a day during Phase II steady state.

Table 7- *Pilot Plant Analytical Monitoring Program*

Parameter	Grab Sample Points (see Figure 1)					
	2	3	4	5	6	7
Free Chlorine		X	X	X	X	
Total Chlorine		X	X	X	X	X
Monochloramine		X	X	X	X	
Dichloramine		X	X	X	X	
Ammonia (NH <sub>3</sub> -N)	X	X	X	X	X	
Ammonia *(after dechlor)	X	X	X	X	X	X
pH	X	X	X	X	X	X
Alkalinity	X					X
Temperature	X					X
Nitrite (NO <sub>2</sub> -N)	X	X				X

\* = after manual dechlorination with sodium bisulfite.

## *Phase I Results and Discussion*

Phase I of the pilot study was designed to provide information on steady state breakpoint pilot operations, and factors which affect its performance. Extensive operational data (see Appendix F, also summarized in Table 8) was collected during three separate pH runs, under steady state conditions, and analyzed to determine which pilot parameters resulted in the best pilot performance.

### **Nitrogen Removal**

The amount of ammonia removal through the pilot plant correlated with changes in pH and contact time, with higher nitrogen/ammonia removal occurring as both of these parameters were increased (see Table 8 and Figure 17). Organic Nitrogen was estimated as the difference between the average TKN & NH<sub>3</sub>-N values for AWT influent and Pilot effluent (see Table 9). Organic-N removal through the breakpoint process was in the range of 19 to 26 percent with the lowest removal occurring at pH 8.0. The results of this pilot study demonstrate that the full-scale breakpoint facility at UOSA (when properly operated) will be able to predictably remove nitrogen/ammonia via the breakpoint process.

Table 8. Data Averages for the pH 7.0, 7.5 and 8.0 runs.

BREAKPOINT PILOT DATA SUMMARY

(Values in mg/L)

SAMPLE POINT	RESIDUAL CHLORINE				PILOT NH3-N	UOSA LABORATORY DATA				SO2:CL Wt. RATIO	Cl:NH3 Wt. RATIO	pH	ALK.	TEMP. C
	Free	Mono	Total	Combined		NH3	TKN	ORG-N	NO2					
INFLUENT	-				11.0	10.8	11.5	0.58			7.1	93	8.8	
R. MIX	-	7.8	5.4	34.8						8.2 : 1	7.0			
10 MIN.	-	6.1	3.0	18.4							6.7			
20 MIN.	-	6.6	0.9	11.7							6.7			
30 MIN.	-	5.8	0.3	8.1							6.7			
30 MIN ON-LINE	-	6.2		8.1										
FINAL EFF.	-				0.25	0.27	0.70	0.43	1.2 : 1		6.5	55	9.6	
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 7.0 RUN)</i>														
INFLUENT	-				11.0	8.9	9.6	0.47			7.7	76	8.5	
R. MIX	-	7.0	1.6	24.4						8.2 : 1	7.5			
10 MIN.	-	5.7	0.4	13.1							6.8			
20 MIN.	-	5.6	0.3	9.2							6.8			
30 MIN.	-	5.4	0.4	7.9							6.8			
30 MIN ON-LINE	-	6.0		8.3										
FINAL EFF.	-				0.18	0.36	0.58	0.37	1.3 : 1		6.6	43	10.3	
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 7.5 RUN)</i>														
INFLUENT	-				11.0	10.8	11.6	0.48			8.8	125	8.0	
R. MIX	-	6.0	6.8	26.4						7.9 : 1	8.0			
10 MIN.	-	3.7	0.6	11.7							7.2			
20 MIN.	-	3.2	0.1	6.5							7.2			
30 MIN.	-	3.3	0.0	5.0							7.2			
30 MIN ON-LINE	-	3.5		5.0										
FINAL EFF.	-				0.12	0.18	0.56	0.39	1.3 : 1		7.0	92	8.1	
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 8.0 RUN)</i>														

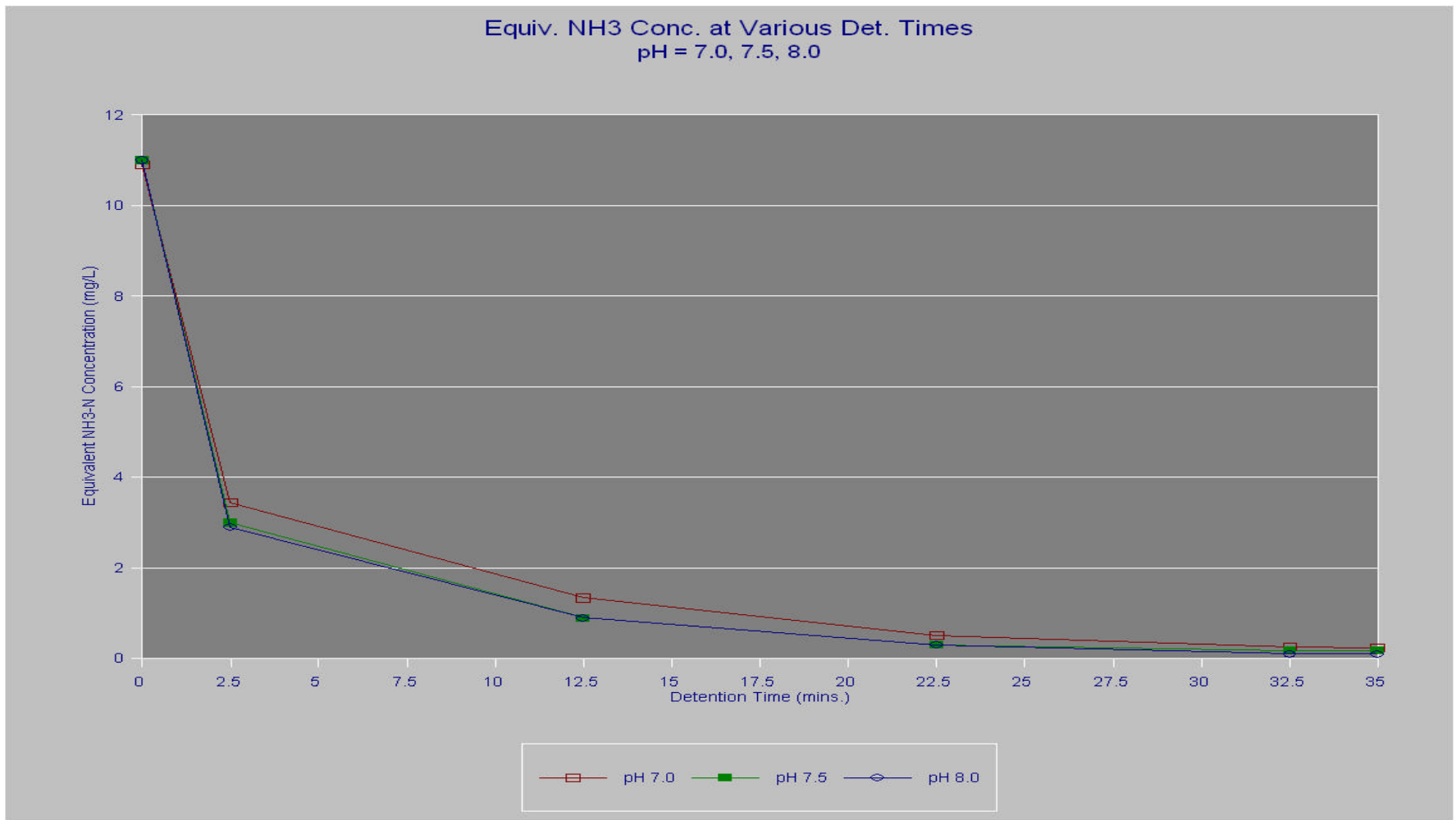


Figure 17. NH3 Disappearance at pH 7.0, 7.5 and 8.0 runs.

Table 9. UOSA Laboratory Averages for the pH 7.0, 7.5, and 8.0 runs.

UOSA Laboratory Analysis of Daily Pilot Plant Composite Samples  
Averages for pH 7.0, 7.5, 8.0

PHASE	TKNH (mg/L)			ORGN (mg/L)			NH3-N (mg/L)			NO2-N (mg/L)			TOTAL OXIDIZED-N (mg/L)		
	AWT EFF.	INFL.	FINAL EFF.	AWT EFF.	INFL.	FINAL EFF.	AWT EFF.	INFL.	FINAL EFF.	AWT EFF.	INFL.	FINAL EFF.	AWT EFF.	INFL.	FINAL EFF.
	#1	#2	#7	#1	#2	#7	1	2	7	1	2	7	1	2	7
pH=7.0															
MIN. -	0.39	10.73	0.35	0.44	0.09	0.07	0.02	10.10	0.12	0.05	0.05	0.05	15.14	13.07	12.05
MAX. -	0.74	12.22	1.17	0.72	0.67	0.96	0.04	11.65	0.53	0.07	0.06	0.05	23.29	25.65	26.44
AVG. -	0.59	11.49	0.70	0.58	0.39	0.43	0.02	10.82	0.27	0.05	0.05	0.05	19.51	20.33	19.67
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 7.0 RUN)</i>															
pH=7.5															
MIN. -	0.12	7.87	0.34	0.10	0.04	0.22	0.02	6.85	0.02	0.05	0.05	0.05	11.68	11.15	10.76
MAX. -	0.68	11.70	0.78	0.66	0.96	0.54	0.04	11.30	0.40	0.05	0.05	0.05	23.99	24.12	24.26
AVG. -	0.49	9.56	0.58	0.47	0.47	0.37	0.02	8.89	0.23	0.05	0.05	0.05	18.06	18.18	18.64
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 7.5 RUN)</i>															
pH=8.0															
MIN. -	0.26	10.66	0.20	0.24	0.07	0.07	0.02	9.85	0.04	0.05	0.05	0.05	10.66	10.00	10.54
MAX. -	0.85	12.08	0.77	0.82	0.88	0.77	0.06	11.70	0.39	0.05	0.10	0.05	23.99	25.78	24.24
AVG. -	0.51	11.58	0.56	0.48	0.50	0.39	0.03	10.85	0.18	0.05	0.05	0.05	17.30	17.40	17.60
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 8.0 RUN)</i>															

## **Reaction Rates**

The rate at which the breakpoint reactions occurred were directly related to the operating pH of the pilot plant. As Figure 18 and Table 8 show, increasing pHs resulted in faster chloramine dissociation throughout the breakpoint pilot. Faster reaction rates resulted during operation at pH of 8.0. Higher pH therefore reduces the contact time required to achieve equivalent ammonia removals. For example it only took ~22 minutes at pH 8.0 to achieve the same effluent ammonia concentration that took ~32 minutes to achieve at a pH of 7.0.

It is recommended that UOSA use NaOH addition in the breakpoint rapid mix vault to insure timely completion of the breakpoint reaction. This is especially important during high flow periods when contact times in the chlorine contact basin are reduced.

## **Weight Ratios**

Chlorine to ammonia dose ratios were approximately 8:1 (see Table 8) for the Phase 1 operations.

It was observed that a slightly higher chlorine dosage was needed, initially, in order to start the breakpoint reaction. Once the breakpoint reaction was underway the chlorine dosage could be reduced to achieve a lower 30 minute total chlorine residual.

It is more cost efficient and the breakpoint effluent is of higher quality when operation of breakpoint is as close to stoichiometric values as possible. It is,

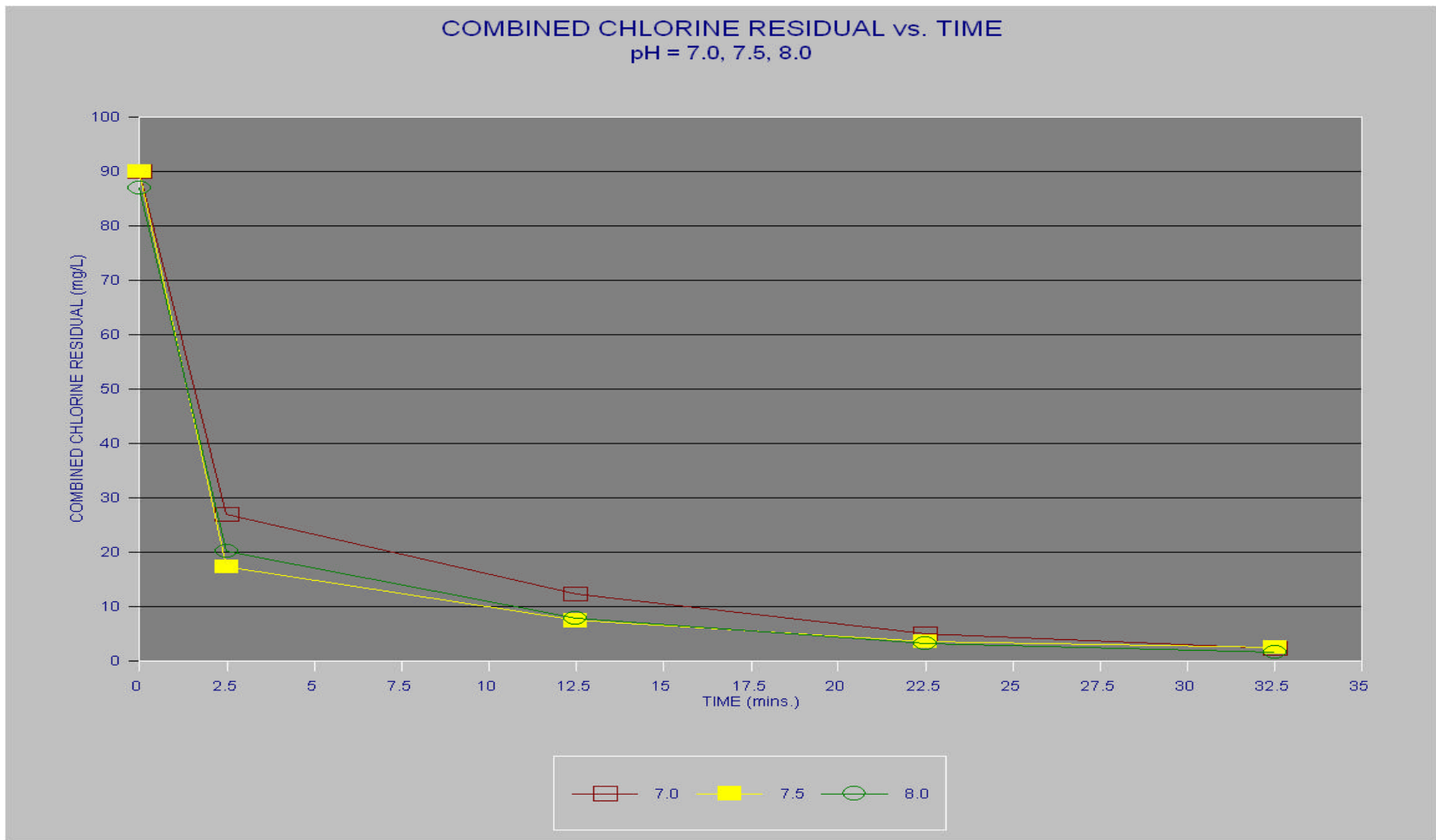


Figure 18. Combined Chlorine Residual disappearance at pH 7.0, 7.5 and 8.0 runs

however, also important to maintain a certain amount of chlorine overfeed to buffer out any instantaneous process perturbations which may cause loss of the breakpoint reaction. Loss of breakpoint results in a poor quality effluent for a period of time until the breakpoint reaction is re-established and the system is flushed out.

### **Process Stability**

Loss of the breakpoint reaction was caused by numerous explainable events, the most common being chlorine underfeed. Underfeed conditions were mostly attributed to operator attempts to lower the  $\text{Cl}_2$ :  $\text{NH}_3$  dose ratio to maintain a 30 minute (contact time) free chlorine residual at the lowest possible concentration that would sustain the breakpoint reaction. Operating the breakpoint pilot at low (< 5.0 mg/L free  $\text{Cl}_2$ ) 30 minute (contact time) chlorine residuals proved more difficult at (rapid mix tank) pH 7.0 than at the other pHs (7.5 and 8). Once the breakpoint reaction was lost at pH 7.0, the 30 minute (on-line analyzer) total chlorine residual value went off scale (see Figure 19) and it required a long period of time to re-establish and optimize the breakpoint reaction. In contrast to this, the increase of the breakpoint operating pH from 7.0 to 7.5 then finally 8.0 resulted in an increasingly more stable breakpoint reaction. Loss of breakpoint at the higher pHs, due to a slight underfeed of chlorine, resulted in a less severe loss of the breakpoint with only a slight rise in the 30 minute on-line chlorine values (see Figure 20), and hence was much easier to re-establish. This apparent increase in the stability of the breakpoint reaction at pH 8.0 allowed for pilot operation at lower 30 minute residuals without fear of losing the breakpoint. The increase in stability of the breakpoint reaction at operating pHs 7.5 and 8.0 was attributed to the NaOH addition necessary to achieve these higher pH setpoints. The NaOH addition could have contributed to the formation of the intermediate compound hydroxylamine, which(as shown by other researchers) may provide a



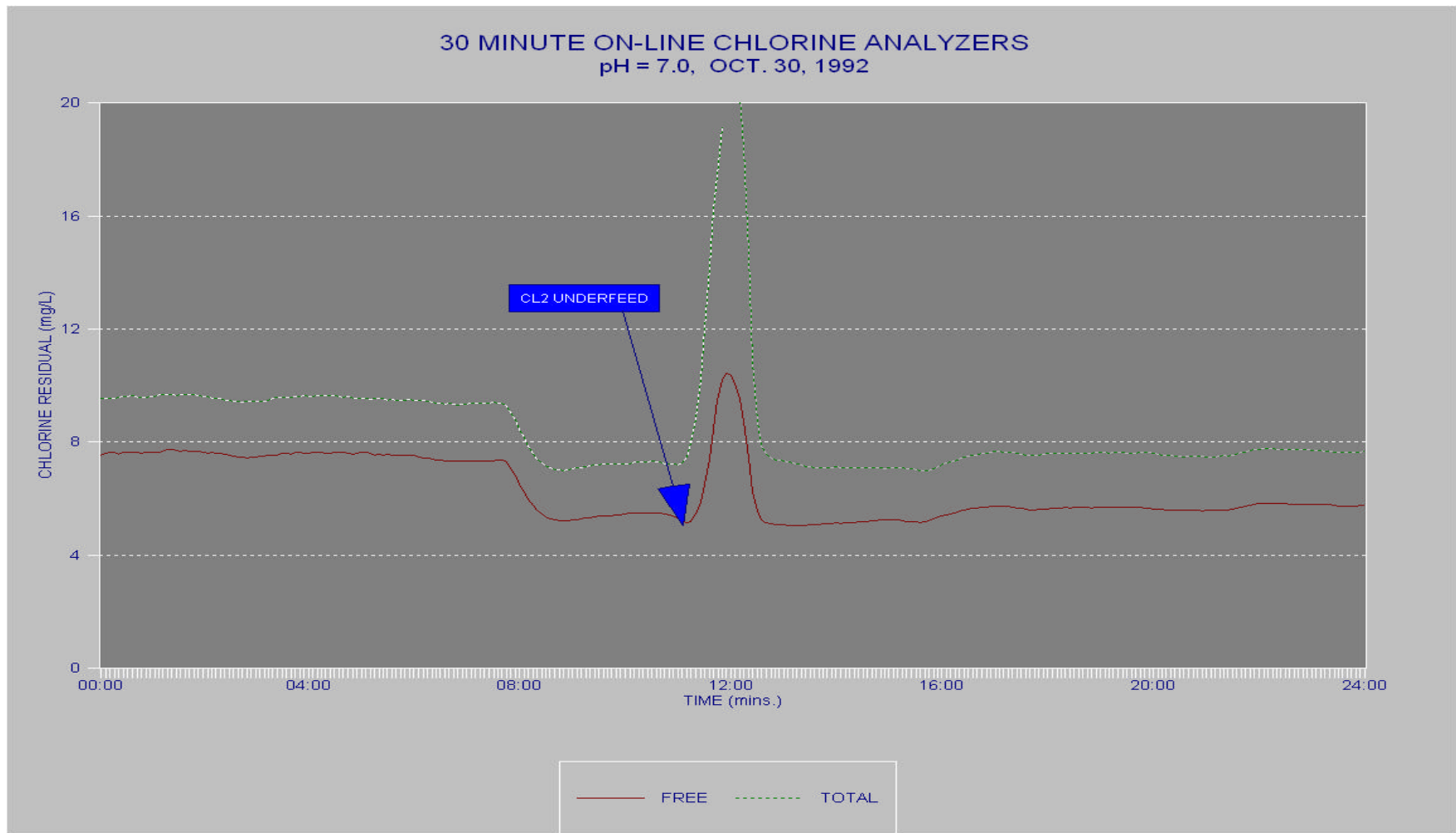


Figure 19. Data Acquisition System Plot of Cl<sub>2</sub> Underfeed and Resulting Loss of Breakpoint

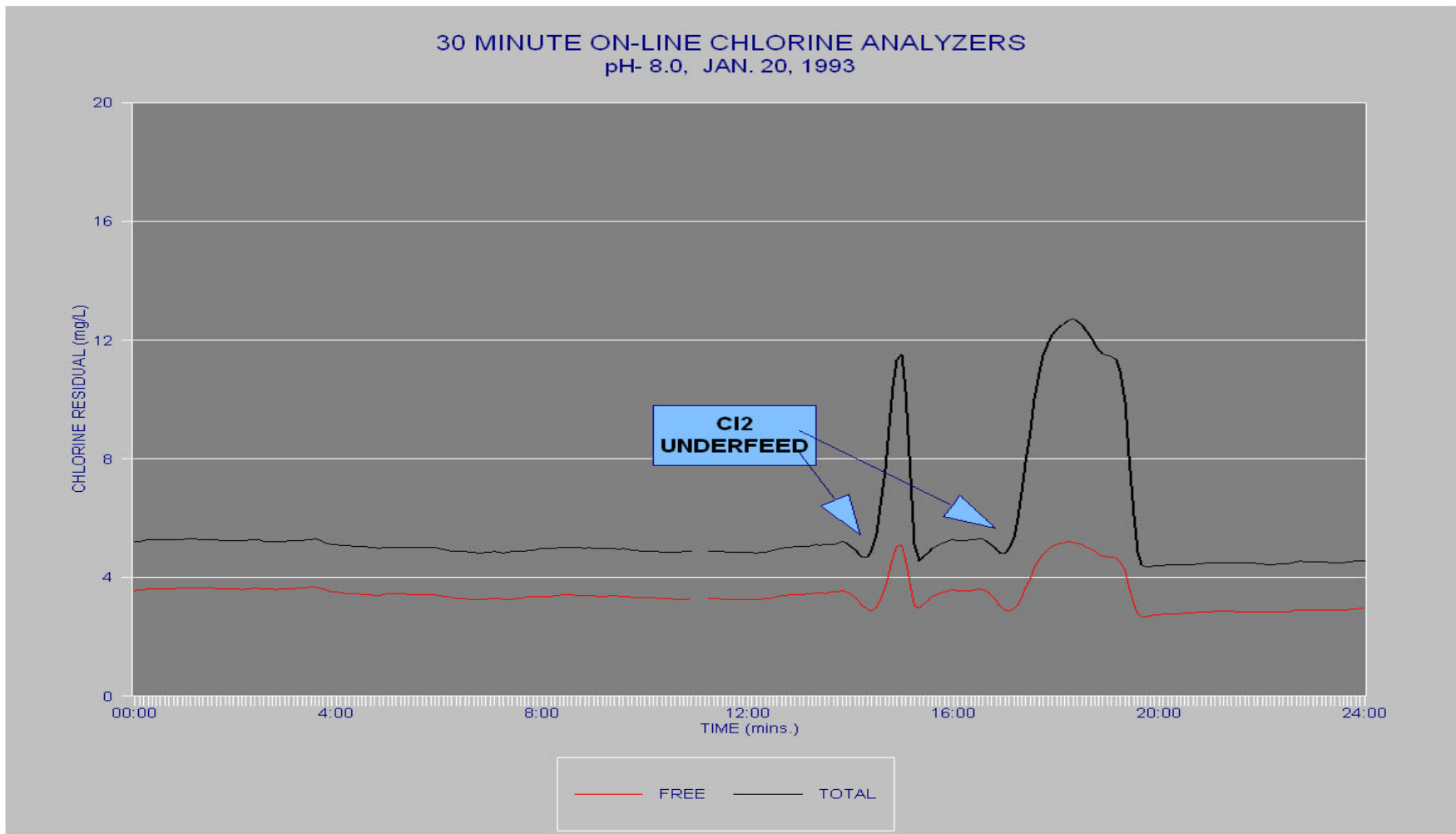


Figure 20. Data Acquisition System Plot of Loss of Breakpoint at pH 8.0

different pathway for completion of the breakpoint reaction. The stability imparted to the breakpoint reaction by the addition of NaOH will allow UOSA to operate the breakpoint process closer to stoichiometric values with more confidence, and allows for quicker recovery of the reaction if it is lost during an underfeed situation.

### **Minimum Chlorine Residuals**

The amount of chlorine needed to maintain the breakpoint reaction varied with the operating pH of the pilot plant. Data show (Figures 21 and 22) that the minimum 30 minute chlorine residuals required to maintain the breakpoint reaction vary from 6-8 mg/L at pH 7.0, to 3-5 mg/L at pH 8.0. These ranges reflect the slight chlorine overfeed necessary to provide a buffer, so that any perturbations encountered during operations would not result in loss of the breakpoint due to chlorine underfeed.

As stated above under Phase I Results and Discussion/Weight Ratios, it is important to maintain a slight chlorine overfeed to insure a continual breakpoint operation. On-line chlorine analyzers are preferred for monitoring the instantaneous concentrations of both total and free chlorine at various points during the breakpoint process. However, if these on-line instruments are being used to provide feedback to a distributed control system it should be noted that there exists a potential for problems that can occur when the loss of breakpoint occurs. The problem is a result of a false free chlorine reading that appears on free chlorine instrumentation during the loss of breakpoint due to a chlorine underfeed situation (Figures 19 and 20). During loss of breakpoint (due to chlorine underfeed) there should not be any free chlorine in the system at all. The

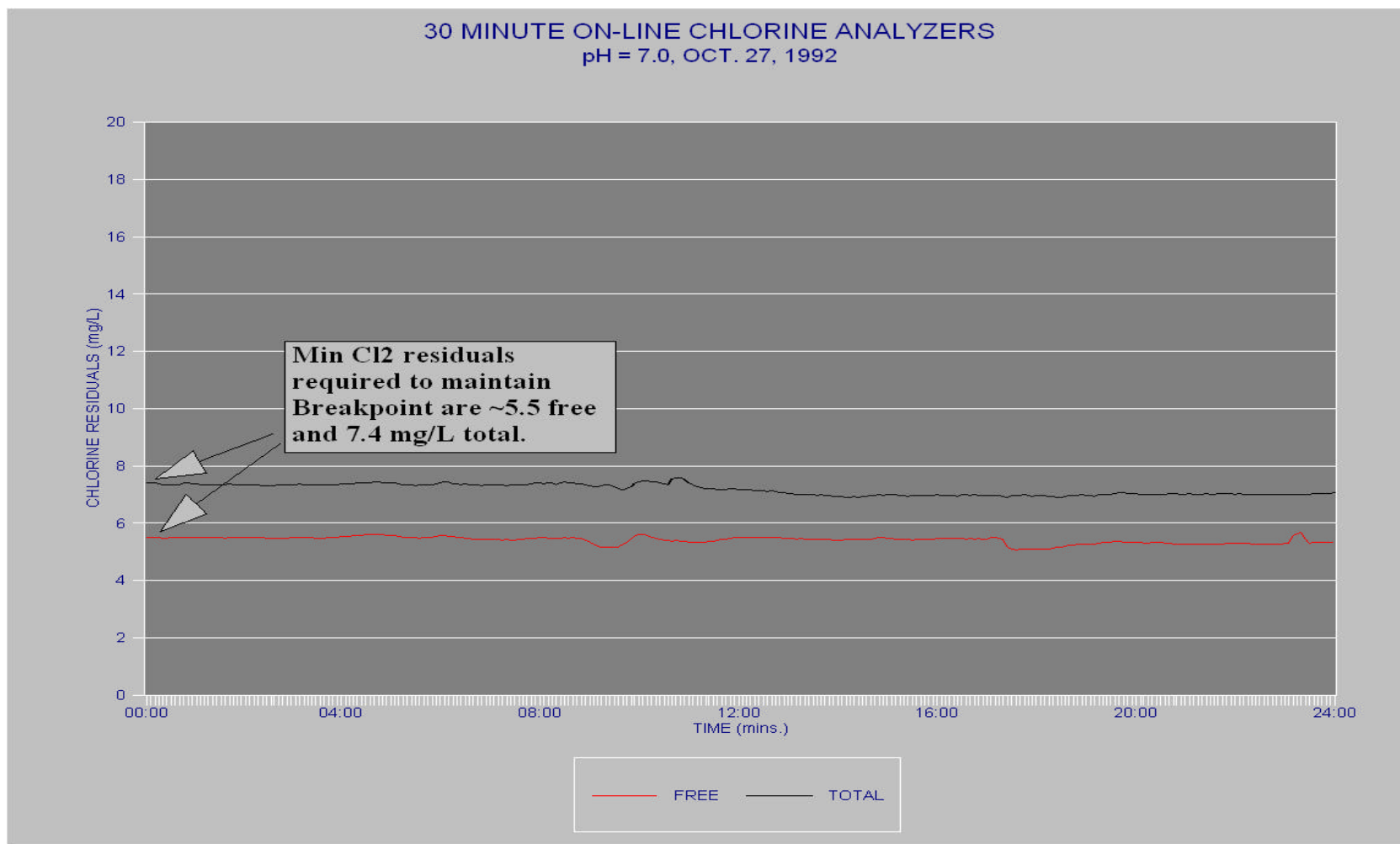


Figure 21. Data Acquisition System Plot of Minimum Cl<sub>2</sub> Residuals Required to Maintain Breakpoint at pH = 7.0.

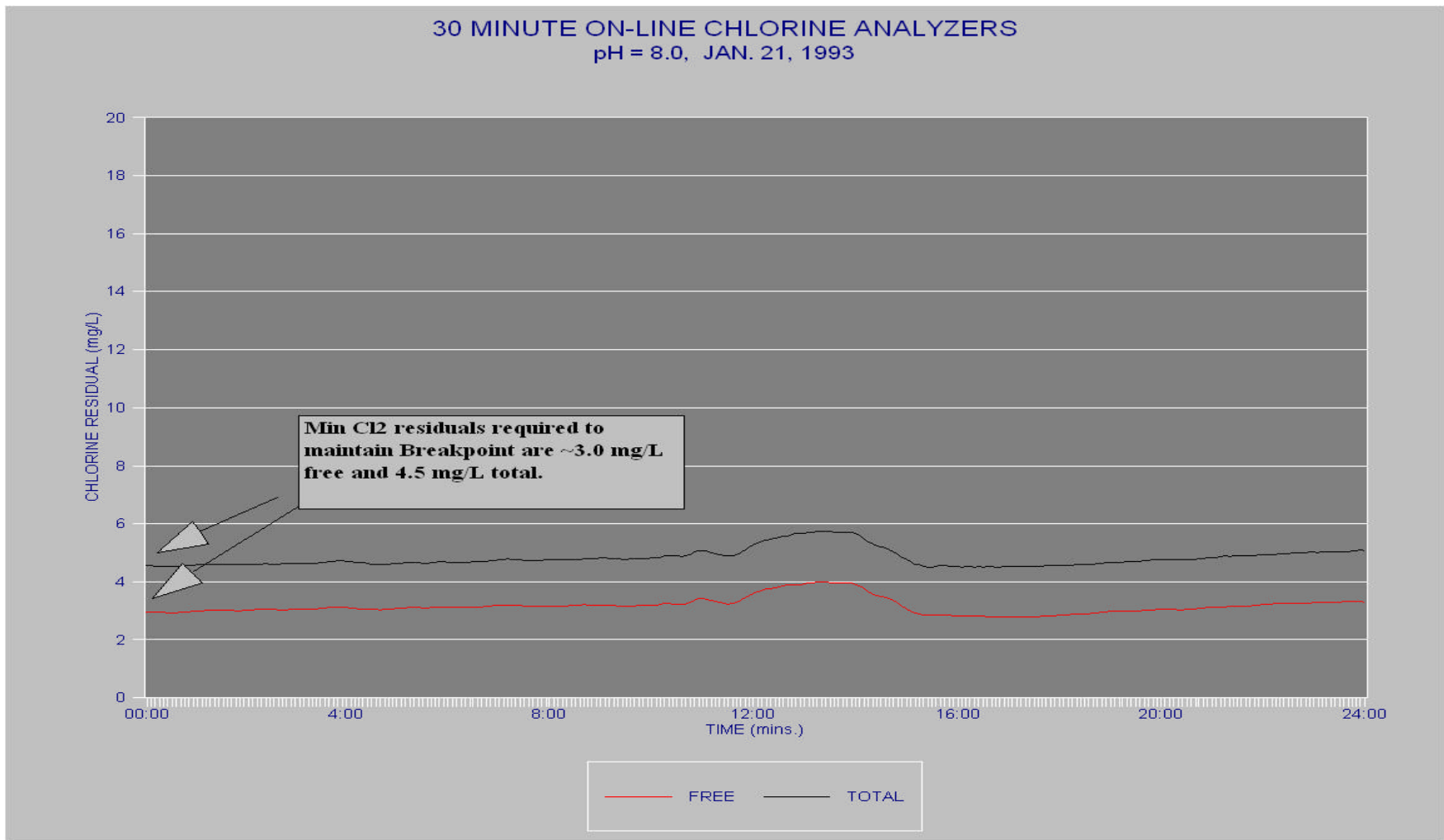


Figure 22. Data Acquisition System Plot of Minimum Cl<sub>2</sub> Residuals Required to Maintain Breakpoint at pH = 8.0

appearance of a false increase in free chlorine by the on-line instrumentation was discussed with the manufacturer of the instrumentation but was never resolved. Changing of free chlorine analyzer buffer solutions from pH 4.0 to 7.0 were discussed but it was not followed up upon due to time constraints.

The presence of false free chlorine will create problems if the breakpoint process is being operated based on free chlorine feedback to a distributed control system algorithm. A breakpoint control algorithm based on free chlorine feedback will want to decrease the chlorine feed in order to maintain the setpoint free chlorine determined by the operator. The control systems attempt to lower the free chlorine by lowering the overall chlorine feed rate only exacerbates the problem of the underfeed situation and can only be corrected by manual intervention or a well thought out algorithm which monitors for this type of situation.

### **Dechlorination**

Dechlorination ( $\text{SO}_2$ ) requirements (see Table 8) were consistent throughout the operation of the breakpoint pilot study. The average dosage was 1.3:1  $\text{SO}_2:\text{Cl}_2$  and did not show any variation within the pH ranges tested. Although it was possible to obtain a lower  $\text{SO}_2:\text{Cl}_2$  ratio, it was also necessary to maintain a slight overfeed or buffer of  $\text{SO}_2$  to compensate for the minor chlorine fluctuations inherent during the daily pilot operations.

UOSA currently has a zero chlorine discharge as part of its Operating Permit. Any measurable discharge of chlorine could be cause for a permit violation as well as be detrimental to aquatic life in the receiving body of water. To insure that chlorine discharge is kept at zero a slight  $\text{SO}_2$  overfeed should be maintained.

## **pH Issues**

pH control for the pilot study was provided with NaOH and was adjusted to obtain the desired pH in the rapid mix tank where chlorine addition occurs (see Figure 16). Although the values obtained in this zone (see Table 8) reflect the breakpoint reaction pH, they are not representative of the pHs in other pilot plant reaction tanks. The amount of NaOH added to maintain the breakpoint rapid mix tank pH at 7.5 and 8.0 resulted in pilot influent pHs of 7.7 and 8.8 respectively. The pH 7.0 run did not require any NaOH addition. As the rapid mix pH of the pilot plant was increased from 7.0 to 8.0 the final effluent pH also increased from 6.5 to 7.0 respectively. The amount of pH drop through the breakpoint pilot increased with increasing rapid mix setpoint pH (see Table 8). This was attributed to rapid consumption of hydroxide alkalinity introduced from NaOH addition to maintain the desired pH setpoint.

## ***Other Parameters Of Interest***

- The COD (chemical oxygen demand) showed a consistent decrease (see Table 10) through the breakpoint pilot plant, with more COD removal occurring as the pH decreased from 8.0 to 7.0.
- Alkalinity consumption was very close to the stoichiometric values (3.6 mg/L alkalinity as CaCO<sub>3</sub> per mg/L NH<sub>4</sub>-N) predicted for the breakpoint reaction (see Table 8).

Disinfection By-Product analysis through the breakpoint pilot plant (see Appendix G) showed consistent increases in Chloroform. It was also noted that Total Organic Halides were being created during the breakpoint process, but at values below concern for drinking water. One sample was

Table 10. UOSA Laboratory Analysis of Pilot Plant Samples for the pH 7.0, 7.5 and 8.0 runs

UOSA Laboratory Analysis of Daily Pilot Plant Composite Samples										
Averages for pH 7.0, 7.5, 8.0										
PHASE	TSS (mg/L)			TS (mg/L)			COD (mg/L)			COLIFORM (CFU/100 ml)
	AWT EFF. 1	INFL. 2	FINAL EFF. 7	AWT EFF. 1	INFL. 2	FINAL EFF. 7	AWT EFF. 1	INFL. 2	FINAL EFF. 7	FINAL EFF. 7
pH = 7.0										
MIN. -				210	140	290	7.0	7.0	3.0	< 1
MAX. -				630	690	850	11.0	10.0	8.0	< 1
AVG. -				454	472	678	9.6	8.6	5.1	< 1
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 7.0 RUN)</i>										
pH = 7.5										
MIN. -	0.0	0.0	0.0	430		770	6.2	5.2	1.8	< 1
MAX. -	0.5	0.3	0.3	560		990	12.0	8.9	8.0	< 1
AVG. -	0.2	0.1	0.1	490		866	8.3	7.3	4.8	< 1
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 7.5 RUN)</i>										
pH = 8.0										
MIN. -				300	200	440	4.0	7.0	5.0	< 1
MAX. -				480	640	690	13.0	11.0	8.0	< 1
AVG. -				404	430	595	8.3	8.2	7.0	< 1
<i>(ABOVE VALUES ARE AVERAGES FOR THE pH 8.0 RUN)</i>										



noted for having a large value detected for *Trichloroacetic Acid*. However, this only occurred once and was not detected in any other samples or subsequent analysis.

- Total solids analysis showed an increase through the breakpoint pilot plant for all pHs studied (see Table 10). However, since the pilot plant was equipped with a 50 $\mu$ m prefilter, located after the chiller, the increase in total solids was attributed entirely to dissolved solids generated from the chemicals used in the reactions
- During pre-startup operations when the breakpoint pilot personnel weren't as knowledgeable in breakpoint process dynamics and pilot operations, and the pilot exhaust fan wasn't turned on, there were observations of a peculiar odor emanating from the pilot plant. This occurred when the chlorine to ammonia dose ratio was known to be greater than optimal, and pH adjustment was not being used. These odors disappeared when the breakpoint reaction was optimized to dose ratios closer to stoichiometric. No odors were reported subsequently.
- Data indicate (Table 9) that nitrate production through the breakpoint pilot plant was minimal. As the literature suggests, nitrate is found only in minor amounts as an end product of breakpoint chlorination at the stoichiometric values that were used during this study.
- There were no fecal coliforms detected in any of the effluent samples tested.

## ***Phase I. Summary and Conclusions***

### **Pilot Operations**

- All pHs provided acceptable operation during steady state operation.
- Slower reaction rates were observed at lower pHs.
- Lower pHs were associated with less stable breakpoint operations.
- Alkalinity consumption was observed close to being stoichiometric.
- Chlorine addition in excess of the  $\text{Cl}_2$  demand plus the stoichiometric amounts required to reach the breakpoint resulted in a corresponding decline in ammonia removal efficiencies.
- Data from pilot operation at higher pHs (7.5 & 8.0) showed :
  - lower 30 minute free and total  $\text{Cl}_2$  residuals,
  - lower effluent  $\text{NH}_3$  and TKN concentrations,
  - $\text{Cl}_2:\text{NH}_3$  closer to stoichiometric,
  - final effluent pH closer to neutrality (i.e. pH ~7.0).

### **Laboratory Data**

- COD removal was observed through breakpoint.
- Minimal  $\text{NO}_3^-$  production was observed during the breakpoint reaction.
- Total Solids increased through the breakpoint process.
- No Fecal Coliforms were detected after 30 minutes contact time in the pilot.

## **DAS Data**

- Loss of breakpoint was observed more frequently at lower operating pHs.
- Loss of breakpoint at higher pHs was not as severe (easier to get back).
- The ability to run at lower free and total chlorine residuals was observed as operating pHs increased from 7.0 to 8.0.
- Numerous unexplained perturbations occurred at pH 7.0, causing loss of breakpoint.
- A more stable breakpoint process was occurred at pH 8.0.

## **DBP Data**

- Consistent increases in *Chloroform* through breakpoint, though not to levels that would jeopardize drinking water sources.
- Creating *Total Organic Halides* through breakpoint, again, not to levels that would jeopardize drinking water sources.

## ***Phase II Results and Discussion***

Data generated during these studies were compared to operational data generated during Phase I (rapid mix pH=8.0, Temp=8 °C, Influent NH<sub>3</sub>-N=11.0 mg/L).

### **Variable Temperature Studies**

The pilot plant was operated for two periods each of 5 day per week, 8 hour per day duration. One week of operation occurred with water temperatures at 12 °C and the other at 20 °C. The third data set used for the 8 °C comparison was collected during Phase I. All of these variable temperature tests were operated with influent NH<sub>3</sub>-N concentrations of 11 mg/L and rapid mix pH of 8.0.

Results of the variable temperature studies showed that better pilot performance (faster oxidation of ammonia) occurred at higher influent temperatures (see Figures 23 and 24). Increased breakpoint reaction rate due to increased influent temperature followed the van't Hoff-Arrhenius rule and was anticipated. Pilot performance was very similar at both 8 and 12 °C. However, the best performance occurred at 20 °C. Chlorine to ammonia dose ratios remained constant at ~8:1 for all three influent temperatures tested. Operational and laboratory data averages are presented in Table 11, and raw data are presented in Appendix E. Due to the indeterminate nature of when breakpoint operations would need to be initiated, UOSA is at the mercy of the water temperature at the time. It is noted, however, that the more desirable conditions for breakpoint operations will generally be during warm-weather months (from May until October) in the Northern Virginia area.

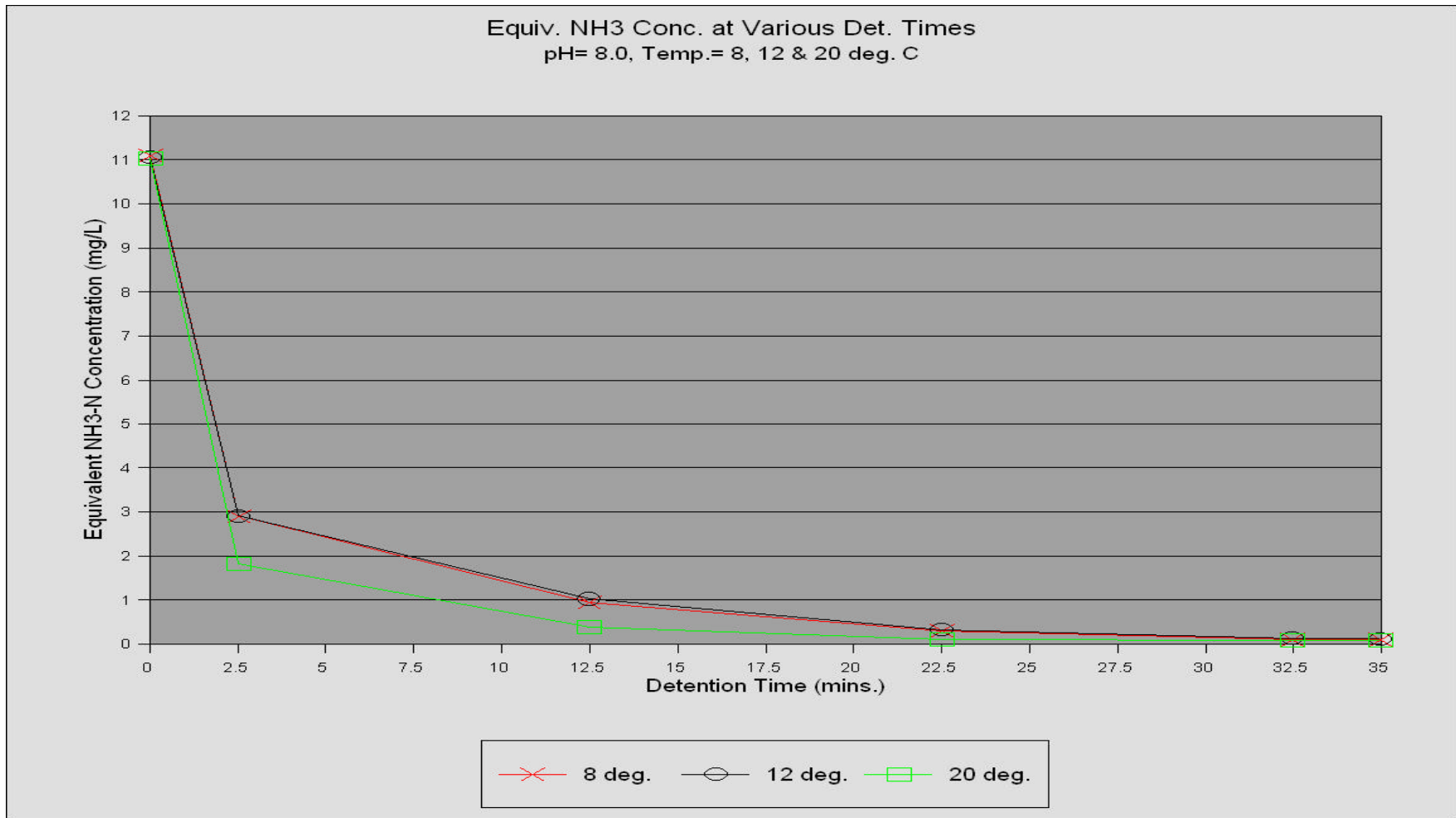


Figure 23. NH3 Concentrations vs. Time at Different Pilot Plant Water Temperatures

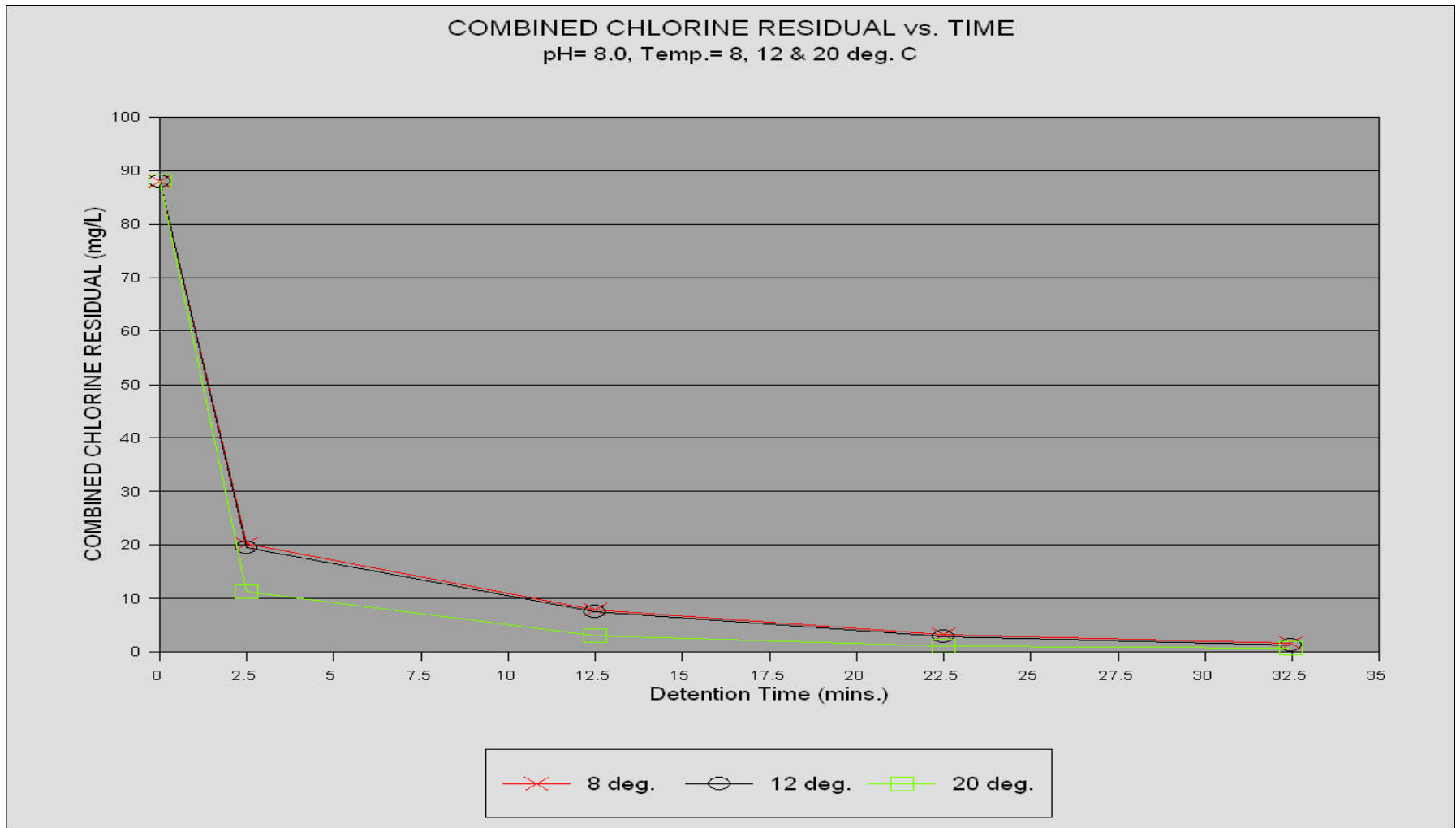


Figure 24. Combined Chlorine Residual vs. Time at Different Pilot Plant Water Temperatures

Table 11. Pilot Plant Averages for 8, 12, and 20 Degree C runs

BREAKPOINT PILOT DATA SUMMARY

Values in mg/L

SAMPLE POINT	RESIDUAL CHLORINE				PILOT NH3-N	UOSA LABORATORY DATA				SO2:CL Wt. RATIO	Cl:NH3 Wt. RATIO	pH	ALK.	TEMP. C
	Free	Mono	Total	Combined		NH3	TKN	ORG-N	NO2					
INFLUENT	-				11.0	10.8	11.6	0.48			8.8	125	8.0	
R. MIX	-	6.0	6.8	26.4						7.9 : 1	8.0			
10 MIN.	-	3.7	0.6	11.7							7.2			
20 MIN.	-	3.2	0.1	6.5							7.2			
30 MIN.	-	3.3	0.0	5.0							7.2			
30 MIN ON-LINE	-	3.5		5.0										
FINAL EFF.	-				0.12	0.18	0.56	0.39		1.3 : 1	7.0	92	8.1	
(ABOVE VALUES ARE AVERAGES FOR THE 8.0 deg. C RUN)														
INFLUENT	-				11.1	11	11.5	0.52			8.9	98.5	12	
R. MIX	-	3.9	6.9	23.3						7.8 : 1	8.1			
10 MIN.	-	2.5	0.8	10.2							7.3			
20 MIN.	-	2.6	0.2	5.5							7.2			
30 MIN.	-	2.8	0	4							7.1			
20 MIN ON-LINE	-	3		6										
FINAL EFF.	-				0.13	0.13	0.56	0.43		1.2 : 1	7.1	57		
(ABOVE VALUES ARE AVERAGES FOR THE 12.0 deg. C RUN)														
INFLUENT	-				11	11.1	12.5	0.7			8.6	107	20	
R. MIX	-	4.2	5.6	15.6						7.9 : 1	8.0			
10 MIN.	-	2.7	0.5	5.9							7.1			
20 MIN.	-	2.4	0.1	3.5							7.1			
30 MIN.	-	2.4	0.1	3.3							7.1			
10 MIN ON-LINE	-	3		6										
FINAL EFF.	-				<.10	0.08	0.56	0.48		1.2 : 1	7.0	74	19.7	
(ABOVE VALUES ARE AVERAGES FOR THE 20.0 deg. C RUN)														

## Variable Ammonia Studies

The pilot plant was operated for two periods, each of 5 day per week, 8 hour per day duration. During one week the pilot plant was operated with an influent  $\text{NH}_3\text{-N}$  concentration of 2.0 mg/L. The other period included operation at 6.0 mg/L  $\text{NH}_3\text{-N}$ . Data collected during Phase I was used for the 11.0 mg/L influent  $\text{NH}_3\text{-N}$  data set. All of these variable influent  $\text{NH}_3\text{-N}$  tests were operated at 8 °C, rapid mix pHs of 8.0 and at a  $\text{Cl}_2\text{:NH}_3$  ratio of 8:1. Variable ammonia studies showed faster ammonia oxidation rate at higher influent ammonia concentrations (see Figure 25 and Table 12). Pilot operation was much easier to control and more stable (less likely to lose breakpoint due to slight  $\text{Cl}_2$  underfeed) at the lower influent ammonia concentrations. Lower pilot influent ammonia concentrations also made it possible to maintain lower total chlorine residuals in the 30 minute contact tank, thus lowering dechlorination requirements.  $\text{SO}_2\text{:Cl}_2$  dose ratios shown in Table 12 for the 2.0 mg/L  $\text{NH}_3\text{-N}$  run is not representative of the actual  $\text{SO}_2$  requirement. An oversized dechlorination pump and turn down limitations of the pump resulted in feeding more  $\text{SO}_2$  than necessary. Operational and laboratory data averages are presented in Table 12. Actual raw data are presented in Appendix E. The amount of ammonia needed to be removed from the wastewater via breakpoint operations is difficult to predict. A slight process perturbation can result in only 1-2 mg/L of residual ammonia needing to be removed. A more severe biological system failure could result in 11mg/L or greater of residual ammonia that will need to be removed via breakpoint chlorination. Ideally, as was shown in the pilot operations, smaller concentrations (1-3 mg/L) of ammonia are much easier and less costly to remove.



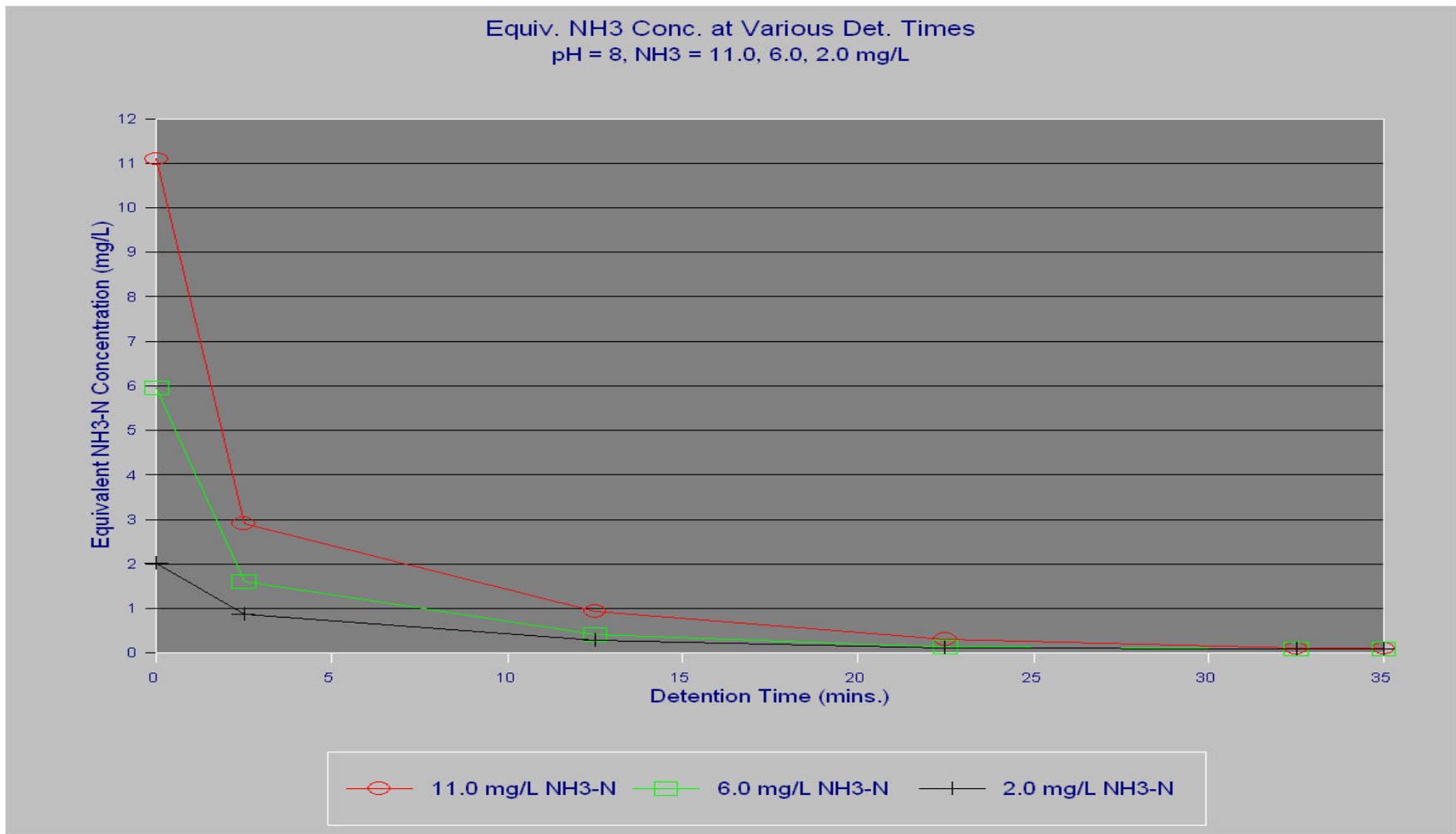


Figure 25. NH3 Disappearance vs. Time for Varying Influent NH3 Concentrations

Table 12. Pilot Plant Averages for the 11.0, 6.0, and 2.0 mg/L NH<sub>3</sub> runs

BREAKPOINT PILOT DATA SUMMARY

Values in mg/L

SAMPLE POINT	DIADIAL CHLORINE				PILOT NH <sub>3</sub> -N	UOSA LABORATORY DATA				SO <sub>2</sub> :CL Wt. RATIO	Cl:NH <sub>3</sub> Wt. RATIO	pH	ALK.	TEMP. C
	Free	Mono	Total	Combined		NH <sub>3</sub>	TKN	ORG-N	NO <sub>2</sub>					
INFLUENT	-				11.0	10.8	11.6	0.48			8.8	125	8.0	
R. MIX	-	6.0	6.8	26.4						7.9 : 1	8.0			
10 MIN.	-	3.7	0.6	11.7							7.2			
20 MIN.	-	3.2	0.1	6.5							7.2			
30 MIN.	-	3.3	0.0	5.0							7.2			
30 MIN ON-LINE	-	3.5		5.0										
FINAL EFF.	-				0.12	0.18	0.56	0.39	1.3 : 1		7.0	92	8.1	
(ABOVE VALUES ARE AVERAGES FOR THE 11.0 mg/L NH <sub>3</sub> -N RUN)														
INFLUENT	-				6.0	6.1	6.5	0.38			8.5	115	8.4	
R. MIX	-	5.0	7.2	20.2						8.1 : 1	8.0			
10 MIN.	-	2.9	0.5	7.9							7.4			
20 MIN.	-	3.0	0.1	4.8							7.3			
30 MIN.	-	3.0	0.0	4.1							7.3			
20 MIN ON-LINE	-	3.0		4.6										
FINAL EFF.	-				0.10	0.13	0.41	0.28	1.4 : 1		7.2	90	8.7	
(ABOVE VALUES ARE AVERAGES FOR THE 6.0 mg/L NH <sub>3</sub> -N RUN)														
INFLUENT	-				2.0	2.1	2.9	0.71			7.8	91	8.0	
R. MIX	-	3.3	2.7	9.6						7.9 : 1	7.8			
10 MIN.	-	2.3	0.4	4.7							7.5			
20 MIN.	-	2.2	0.1	3.3							7.5			
30 MIN.	-	2.1	0.0	2.8							7.4			
20 MIN ON-LINE	-	2.1		3.2										
FINAL EFF.	-				0.10	0.07	0.5	0.43	*3.1 : 1		7.3	83	8.1	
* = NOT REPRESENTATIVE OF ACTUAL REQUIREMENTS														
(ABOVE VALUES ARE AVERAGES FOR THE 2.0 mg/L NH <sub>3</sub> -N RUN)														

### **Increased Organic Nitrogen Concentration**

The pilot plant was operated for a period of 5 days (8-hours per day) at influent Org-N (Organic Nitrogen) concentrations of ~ 1.0 mg/L. Performance of the pilot with influent Org-N concentrations of ~1.0 mg/L was similar to the pilot performance with influent Org-N concentrations of 0.5 mg/L (see Figure 26). Results (Table 13) show average Org-N removal of 40% during elevated Org-N influent operation. This is high in comparison to the average Org-N removals (19-26%) observed in Phase I. This increase in Org-N removal may be due to the presence of easily oxidizable organics present in organic filter press effluent, which was used to spike the pilot influent with Org-N. In comparison, the unspiked UOSA AWT effluent is more likely to contain refractory organics, which can not be either oxidized or adsorbed by UOSA's treatment process. The results (Table 13) also show an increase in  $\text{Cl}_2:\text{NH}_3$  dose ratio required to reach breakpoint at elevated influent Org-N concentrations. This dose ratio increase may be due to the increased  $\text{Cl}_2$  demand imparted to the water after being spiked with the organically rich filter press filtrate. Data also show an increase in the  $\text{SO}_2:\text{Cl}_2$  dose ratio needed to dechlorinate the effluent of the pilot during elevated Org-N testing. This increase was attributed to the formation of organic chloramines which are very persistent and stable in water and more difficult to dechlorinate with sulfite compounds. The disinfection by-product results for this period (see Appendix G) showed slight increases in TOXs and Purgeable Halocarbons/Aromatics through the pilot study. These increases were similar to those observed during the Phase I studies. There was, however, a noticeable increase in Chlorinated Disinfection Byproducts/Haloacetic Acids (HAA) (see Appendix G) when the water was spiked with filtrate, as compared with the earlier studies during Phase I. The HAA increase may be directly related to the addition of organics in the pilot influent, which may not otherwise be present following

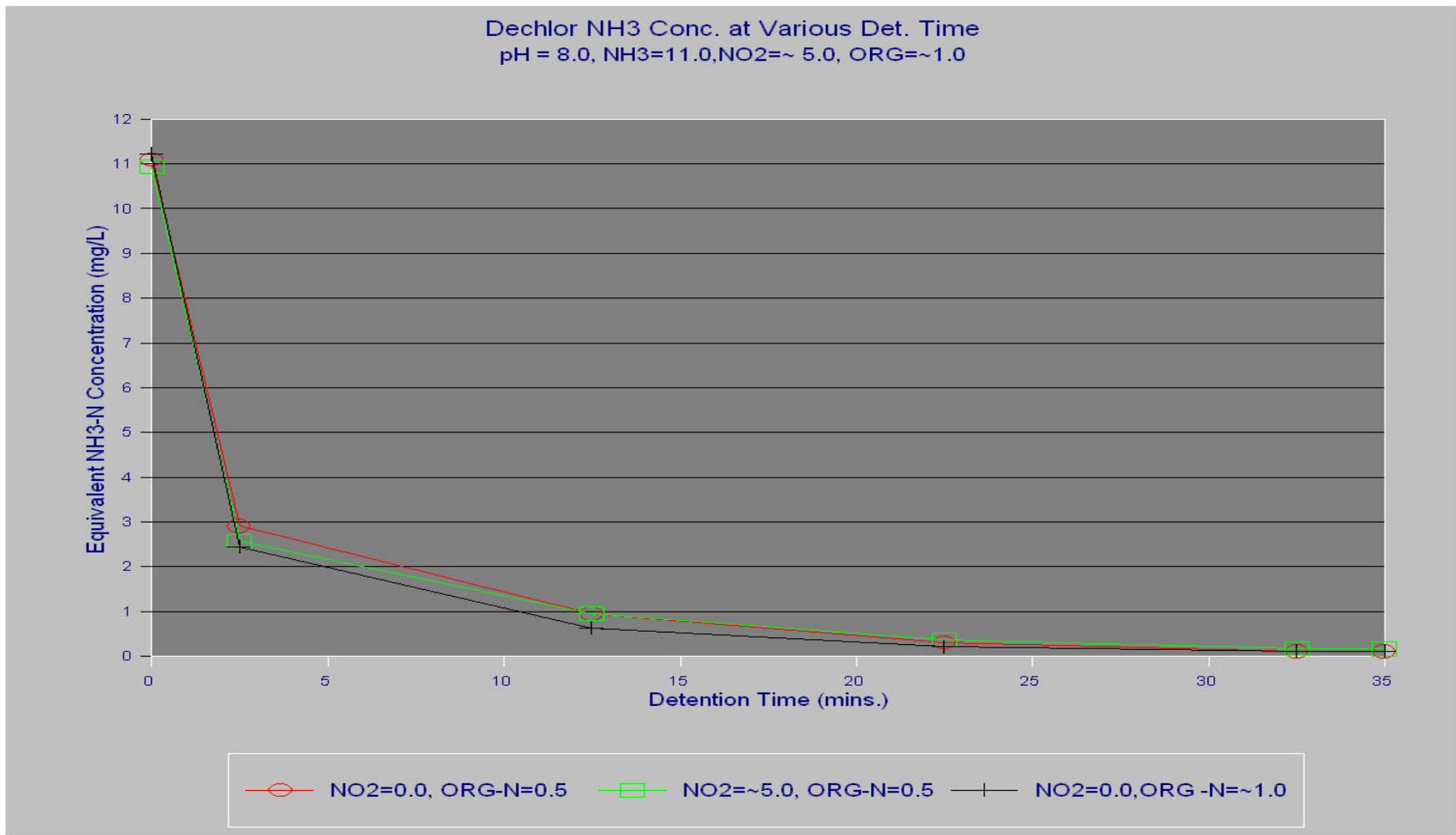


Figure 26. NH<sub>3</sub> Concentrations vs. Detention time for Increased NO<sub>2</sub> and ORG-N runs

Table 13. Pilot and UOSA Lab Averages of 11.0 mg/L NH3-N, 5.0 mg/L NO2-N, and 1.0 mg/L ORG-N runs

BREAKPOINT PILOT DATA SUMMARY															
Values in mg/L															
SAMPLE POINT	RESIDUAL CHLORINE				PILOT NH3-N	UOSA LABORATORY DATA					SO2:CL Wt. RATIO	Cl:NH3 Wt. RATIO	pH	ALK.	TEMP. C
	Free	Mono	Total	Combined		NH3	TKN	ORG-N	NO2	COD					
INFLUENT	-				11.0	10.8	11.6	0.48							
R. MIX	-	6.0	6.8	26.4								7.9 : 1			
10 MIN.	-	3.7	0.6	11.7											
20 MIN.	-	3.2	0.1	6.5											
30 MIN.	-	3.3	0.0	5.0											
30 MIN ON-LINE	-	3.5		5.0											
FINAL EFF.	-				0.12	0.18	0.56	0.39			1.3 : 1		7.0	92	8.1
(ABOVE VALUES ARE AVERAGES FOR THE 11.0 mg/L NH3-N RUN)															
INFLUENT	-				10.9	11.3	11.9	0.48	5.5						
R. MIX	-	4.3	6.9	26.1								10.0 : 1			
10 MIN.	-	3.0	0.5	11.8											
20 MIN.	-	3.5	0.1	6.8											
30 MIN.	-	3.5	0.0	5.4											
20 MIN ON-LINE	-	4.0		6.1											
FINAL EFF.	-				0.18	0.18	0.60	0.41	0.05		1.5 : 1		6.8	54	8.1
(ABOVE VALUES ARE AVERAGES FOR THE 5.0 mg/L NO2-N RUN)															
INFLUENT	-				11.2	11.2	12.2	0.94		12.4					
R. MIX	-	4.4	6.8	26.1								8.3 : 1			
10 MIN.	-	3.1	0.3	9.4											
20 MIN.	-	3.4	0.0	5.8											
30 MIN.	-	3.4	0.0	4.8											
20 MIN ON-LINE	-	3.4		5.1											
FINAL EFF.	-				0.12	0.13	0.70	0.57		10.0	2.7 : 1		7.1	100	8.1
(ABOVE VALUES ARE AVERAGES FOR THE 1.0 mg/L ORG-N RUN)															

UOSAs granular activated carbon process. Operational and laboratory data are located in Appendix G. The amount of organics remaining in the UOSA wastewater after secondary treatment (during a biological upset) is difficult to predict. It is certainly a function of numerous factors, the main one being process efficiency (removal) before reaching the breakpoint vault. Every effort should be made to insure optimum treatment of the wastewater before breakpoint operations begin.

### **Increased Nitrite Concentration**

The pilot plant was operated for a period of 5 days (8-hours per day) at influent nitrite-nitrogen concentrations of ~5.0 mg/L. Performance of the pilot with  $\text{NO}_2\text{-N}$  concentrations of ~5.0 mg/L was similar to pilot operations without  $\text{NO}_2\text{-N}$  (see Figure 26). The results (Table 13) show an increase in the  $\text{Cl}_2\text{:NH}_3$  dose ratio needed to reach the breakpoint. The dose ratio increase was a result of the excess chlorine needed to oxidize  $\text{NO}_2$  and was anticipated. The excess chlorine dosage during this period of operation (Table 13) correlated with the stoichiometric (5:1 weight ratio  $\text{Cl}_2\text{:NO}_2$ ) dose required for oxidation of  $\text{NO}_2$  with  $\text{Cl}_2$ . Oxidation of  $\text{NO}_2$  was immediate and after 2.5 minutes of reaction time all nitrite was completely oxidized. Table 13 shows that pilot final effluent pH during elevated  $\text{NO}_2\text{-N}$  concentrations was slightly lower than encountered for other pilot operations. This pH decrease was not explained by alkalinity consumption, which was also close to stoichiometric. Operational and laboratory data are located in Appendix F.

Increased nitrite concentrations are often a result of incomplete nitrification and are neither predictable nor preventable. UOSA will need to be ready to increase the chlorine:ammonia dose rate to compensate for any nitrite that may be present in the wastewater at the time of breakpoint operations.

## *Phase II Summary and Conclusions*

Analysis of pilot plant and laboratory data generated for this phase of the pilot study revealed:

- 1) Higher pilot operating temperatures (20 °C) resulted in faster reaction rates and lower final effluent ammonia concentrations. All temperatures provided acceptable VPDES permit levels for TKN at steady state operation.
- 2) Higher pilot influent ammonia concentrations (11 mg/L) resulted in faster ammonia oxidation rates, however, lower influent ammonia concentrations (2.0 mg/L) resulted in a more stable pilot operation. Final effluent ammonia concentrations were the same for all three influent ammonia concentrations tested.
- 3) Increased pilot influent organic nitrogen concentrations caused an increase in  $\text{Cl}_2:\text{NH}_3$  dose ratio requirements,  $\text{SO}_2:\text{Cl}_2$  dechlorination requirements, and disinfection byproduct formation. During a full-scale breakpoint operation, the water would pass through all of UOSA's treatment processes reducing the organic load before it reached the breakpoint vault.
- 4) Increased pilot influent nitrite concentrations required higher chlorine feed rates in order to oxidize the  $\text{NO}_2$  present. Operationally, it required ~5mg/L of chlorine (in excess of that

required for breakpoint) to oxidize each mg/L of nitrite present. This was very close to the stoichiometric requirement predicted in the literature. Final effluent pH was slightly lower than normal during this period of operation.



## ***Overall Conclusions and Recommendations***

The research for this study took place over a two year period. Operational information gained throughout this study was used to design and construct a full scale 32 MGD Breakpoint Facility on site at the Upper Occoquan Sewage Authority plant in Centreville VA. The breakpoint pilot study provided an opportunity for UOSA operations group to gain daily operational experience and familiarity with the breakpoint reaction and associated factors which affect successful operation and control of this little used chemical process. The ability to control the breakpoint reaction and effectively remove ammonia or nitrogen reliably and predictably on an as needed basis has provided UOSA with a reliable backup process for its nitrification system. UOSA has gained a comprehensive understanding of the factors which affect the 24 hour a day operation of a breakpoint facility, something that has yet to be presented in the literature.

Although the information gained in this study has proven invaluable to UOSA, it must be noted that the information is specific to UOSA effluent. As noted previously in this study UOSA is not a typical wastewater treatment plant. The extremely high quality effluent that is produced by the UOSA processes, and the use of sodium hypochlorite as a chlorine source, allow for a more predictable and controllable breakpoint operation than would typically be expected in the wastewater treatment industry. Wastewater with less advanced treatment will not likely provide the same results as evidenced in this study. This study should, however, provide the proper ground-work for incorporation of breakpoint facilities at other wastewater treatment plants as long as the caveats above are understood, and plant specific studies are performed to determine chlorine demand, dose ratios, required detention times, proper rapid mixing intensities, etc.....

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## Vita

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