CHLORINE RESIDUAL MEASUREMENT IN CHLORAMINATED SYSTEMS

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ABSTRACT

Melbourne Water operates two treatment plants that employ chloramination as the disinfection process. Chloramines are used due to the long distribution systems these plants service. Several improvement areas in these treatment plants were identified to enable greater control in the operation of the disinfection processes. One of these improvement areas was in the operational monitoring of monochloramine and free ammonia, in addition to chlorine (free and total) residuals. As part of the investigation work, it was found that the indophenol method for measuring monochloramine residual was the most reliable method available and has since been adopted in the field. Extended use of this indophenol method has shown that samples are sometimes providing a monochloramine result that is greater than the DPD total chlorine result, and that the reaction time of the test can have a marked effect on the magnitude of the results. Although more investigation into these test interferences is required, the new testing regime is already providing distinct benefit to the plant operation.

1.0   INTRODUCTION

Melbourne Water operates two chloramination disinfection plants which supply water to separate distribution networks with long retention times, due to the advantages of chloramines compared to free chlorine in such distribution systems. For each of these disinfection plants, chloramination is achieved by flow-paced dosing of aqueous ammonia and chlorine gas.
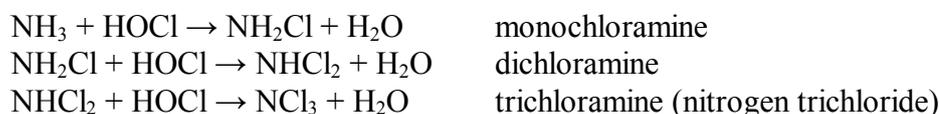
A process review of these disinfection plants has been conducted, and several areas for operational improvement were identified. The objectives of this project were to optimise the use of chlorine and ammonia used in these disinfection plants and to provide greater confidence that the performance of these plants is at the level that Melbourne Water and our customers expect.

As part of this project, an investigation into the testing methods used to measure disinfectant residuals revealed limitations due to analysis interferences and potential inaccuracies. This paper focuses on the investigations into monitoring for operational control and the findings which were incorporated into the operating procedures.

2.0   DISCUSSION

2.1   Chloramine Formation

Chlorine gas dissolved in water forms hypochlorous acid (HOCl). Chloramine formation requires the mixing and chemical reaction between ammonia (NH_3) and the hypochlorous acid. Depending on the stoichiometric ratio of chlorine to ammonia present in the water, the ammonia's hydrogen atoms are substituted with the chlorine atoms. The reaction equations are listed below (White, 2010):

$NH_3 + HOCl \rightarrow NH_2Cl + H_2O$ monochloramine
$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$ dichloramine
$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O$ trichloramine (nitrogen trichloride)

As the concentration of hypochlorous acid increases compared to the ammonia (as nitrogen) concentration, monochloramine is formed until a stoichiometric ratio of 1:1, or 5:1 by weight, is reached. That is, all of the ammonia has been converted into chloramines. As more chlorine is added, dichloramines are formed, followed by trichloramine (nitrogen trichloride). Monochloramine is the desired chloramine, as dichloramine and trichloramine are less stable and have a distinctly offensive odour (NHMRC, NRMMC, 2011). Figure 1 below is the chlorine breakpoint curve which shows the measured chlorine residual changing with an increasing chlorine dose and constant ammonia concentration. The chart is divided into three sections. For chloramine disinfection, the main focus is on Sections I and II of the curve.
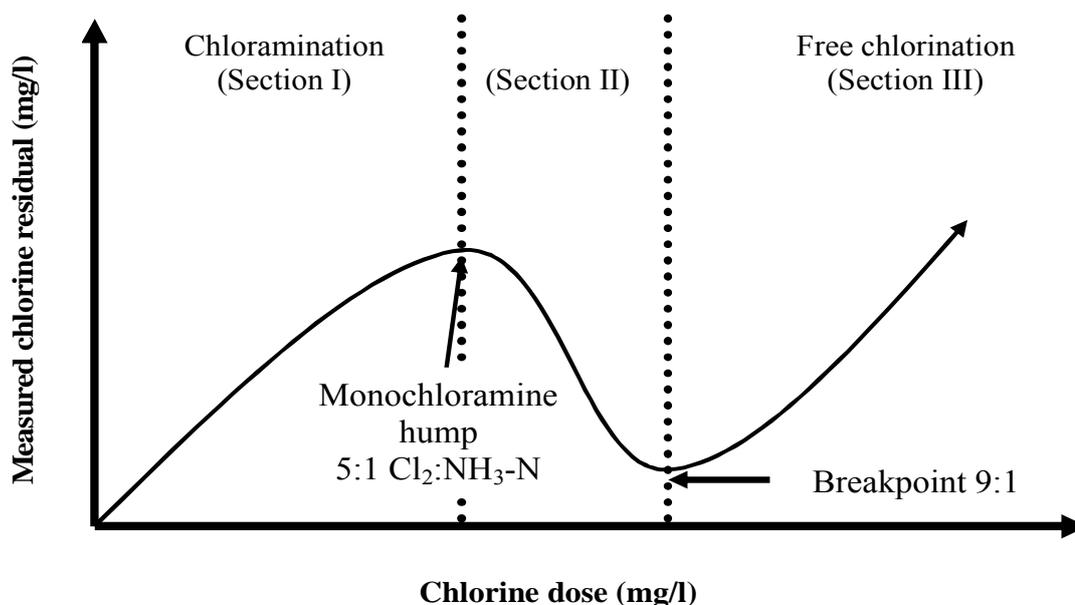

Figure 1: *Representation of the chlorine breakthrough curve, with the measured chlorine residual versus the chlorine dose (adopted from White, 2010)*

The first part of the curve (Section I) is where the ammonia and hypochlorous acid react to form monochloramine (organic and inorganic) and is the desired operating section of the chlorine breakthrough curve. Operationally, for monochloramine formation the optimal pH is 8.4, with an accepted operating range between 7.5 – 9.0 and a chlorine to ammonia (as nitrogen) weight ratio of 3:1 to 5:1. In theory, monochloramines are formed within a few seconds (USEPA, 1999) and the monochloramine concentration (including organic monochloramines, if present) is equal to the total chlorine concentration. Free chlorine measurements should be almost zero as the free chlorine is used in the formation of monochloramine. Free ammonia concentrations will be present until the ratio of chlorine to ammonia (as nitrogen) reaches 5:1, and it is completely consumed.

In Section II, free ammonia has been completely converted to monochloramine. At chlorine to ammonia (as nitrogen) ratios greater than 5:1, the excess chlorine is used in the formation of dichloramines, followed by trichloramines. Therefore, the monochloramine concentration should be less than the total chlorine concentration. Free chlorine measurements should be equal to zero. Any detection of free chlorine residual is actually due to the breakthrough of chloramines into the free chlorine test method (also indicated by an unstable and increasing concentration) (HACH, 2009a).

Breakpoint is reached when the chlorine to ammonia (as nitrogen) ratio is equal to 9:1.

At this point and beyond, all of the free ammonia has been consumed and a free chlorine residual can be measured legitimately. Additionally, the monochloramine concentration will be equal to zero.

2.2   Chloramine Test Methods

To monitor chloramine production, knowing where the treatment plant was operating on the chlorine breakthrough curve was important. Therefore, testing was also important particularly for chlorine (free and total), monochloramines, and free ammonia. Historically, only free and total chlorine residuals were measured, and the discrepancy between the two results indicated the presence of chloramines. Although possible to conduct field tests to separate out the monochloramine, dichloramine and trichloramine concentrations, this was not routinely done. There was also some scepticism in the test methodology, as the calculated chloramine results were usually greater than the total chlorine residual measured, which further prompted investigative work into the testing methods and interferences. Ammonia, nitrate and nitrite were also monitored routinely by external laboratory service providers, however, these tests were also found to be subject to interferences.

The DPD free and total chlorine powder pillow method had historically been used in field testing. Free chlorine measurements in high monochloramine concentration waters were found to be inaccurate, as chloramines breakthrough and erroneously contribute to the free chlorine residual measurement (HACH, 2009a). Additionally, other parameters such as manganese or organic chloramines can influence the readings. Free chlorine concentration readings were also found to increase slowly in the presence of monochloramines. Additives could be included in the test methods to mitigate the effects of these interferences (HACH, 2009a), however, this was seldom done in the field.

The DPD total chlorine powder pillow reagent reacts with all chlorine species, free and combined, organic and inorganic, to give a total chlorine residual. The main issue with the total chlorine residual measurement was that it did not discriminate between different chlorine species (e.g. monochloramine, dichloramine, organic chloramines, etc.) and measured all chloramines, including the organic chloramines which did not provide a disinfection residual (Lee *et. al,* 2007).

The APHA Standard Methods (2005) DPD colorimetric method for chloramines was similar to the DPD free and total chlorine methods above. However, it was able to distinguish between the different chloramines with staged addition of a potassium iodine (KI) catalyst after the DPD free chlorine measurement step. As per the free chlorine measurement, the presence of monochloramines interfered with the result making the test unreliable. Dichloramines and trichloramines could also potentially breakthrough into the monochloramine, as results were very dependent on the chlorine to ammonia ratio, which determined the amount of KI to be added. At a ratio of 5:1 the monochloramine concentration varied from 10-15%, whereas when the ratio was less than 5:1 the error was found to be up to 30% different compared to the indophenol method (outlined below). Therefore, the ratio needed to be known before doing the test in the field.

The HACH Monochlor F indophenol method (HACH, 2009b) was used to measure the monochloramine, and could also measure the free ammonia concentration. The reagent selectively reacted with the two hydrogen atoms present on the monochloramine molecule to form an indophenol which was proportional to the monochloramine residual.

The free ammonia concentration was determined by adding a reagent containing hypochlorite to a separate sample, which combined with free ammonia converting it to monochloramine. The monochloramine residual was measured directly from the sample without the reagent addition, and the free ammonia was calculated as the difference between the results of the two samples.

Other ammonia test methods such as the salicylate powder pillow, phenate and Nessler methods for determining the ammonia concentration were all affected by the presence of chloramines and should not be used for chloraminated waters as each involve converting the ammonia into chloramines and measuring their concentration (APHA *et. al*, 2005).

From the investigation into the monitoring methods, the only reliable method for determining the monochloramine concentration was found to be the indophenol method. Interferences from chloramines in the DPD powder pillow method for determining the free chlorine concentration, and monochloramine concentration, significantly impacted the results making them unreliable.

2.3   Monitoring Data

Figure 2 below shows the data collected since implementing the monochloramine residual monitoring. The sample point was at the treatment plant, post-treatment. Total chlorine was measured using the DPD total chlorine powder pillow method, whereas the monochloramine residual and free ammonia were measured using the HACH Monochlor F method. The fraction of monochloramine present was calculated by dividing the monochloramine residual by the total chlorine residual.
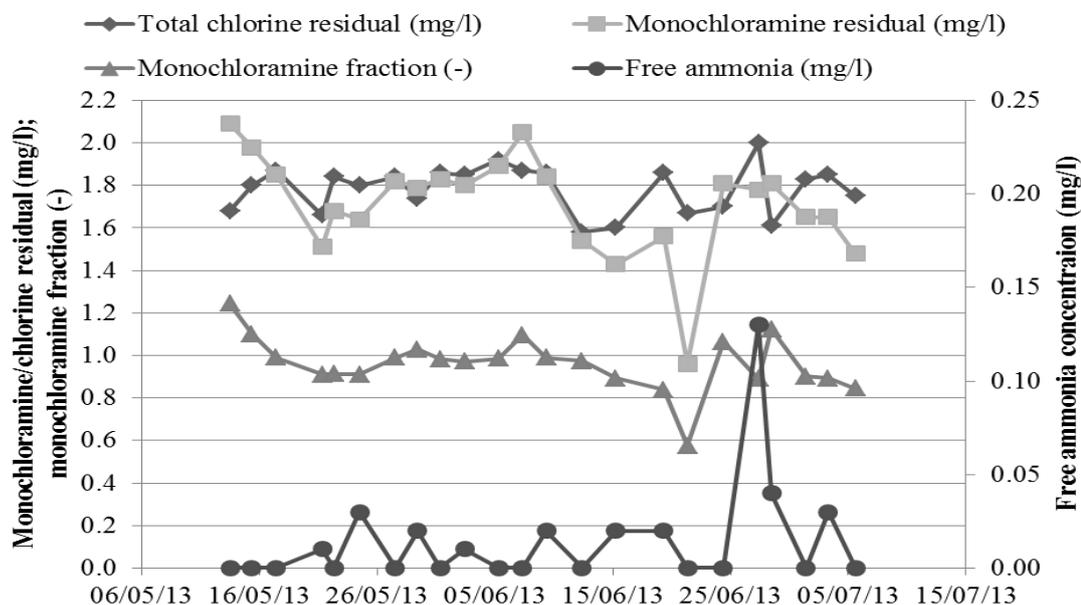

Figure 2:   *Monochloramine, total chlorine, monochloramine fraction and free ammonia monitoring data results measured at the treatment plant post-treatment*

The data show that the chloramination plant has been operating at around the set point of 1.8 mg total chlorine/L. The data also show that the plant has been able to control the ammonia dosing to the expected level and monochloramines were the dominant chlorine species.

A rise in the free ammonia concentration when the monochloramine residual was lower occurred as expected by the chlorine breakthrough curve theory. However, from the data shown, inaccuracies were present as occasionally the monochloramine fraction was greater than 1, which was not practically possible. On one occasion, the monochloramine fraction was 57% which was due to the plant being offline. It was unclear why the free ammonia concentration spiked to 0.13 mg/l on one occasion. Despite these anomalies, the monochloramine residual testing has enabled the ability to readily and easily monitor the monochloramine and ammonia concentration in the field where adjustments could be made on the spot.

2.3   Issues With Chloramine Test Method Reaction Times

As shown in Figure 2, there were some issues in the testing. The water chemistry such as pH or temperature could also have affected the residual measurements as well as the test kit accuracy, both in the monochloramine test kit and total chlorine test kit. According to the method manual, depending on the water temperature, different reaction times are required (HACH, 2009b). Operators routinely using the monochloramine test kit to measure monochloramine and free ammonia found that if the monochloramine residual was measured either before or after the given reaction time for the sample temperature, then there would be a discrepancy in the results. To test these discrepancies, a series of samples were taken from a sample tap on the inlet to the storage tank. The source water temperature at the time was approximately $16^{o}C$. According to the test kit manual (HACH, 2009b) the reaction time at this temperature should be 6 minutes. The monochloramine residual was measured after several different reaction times. The results are shown in Figure 3 below:
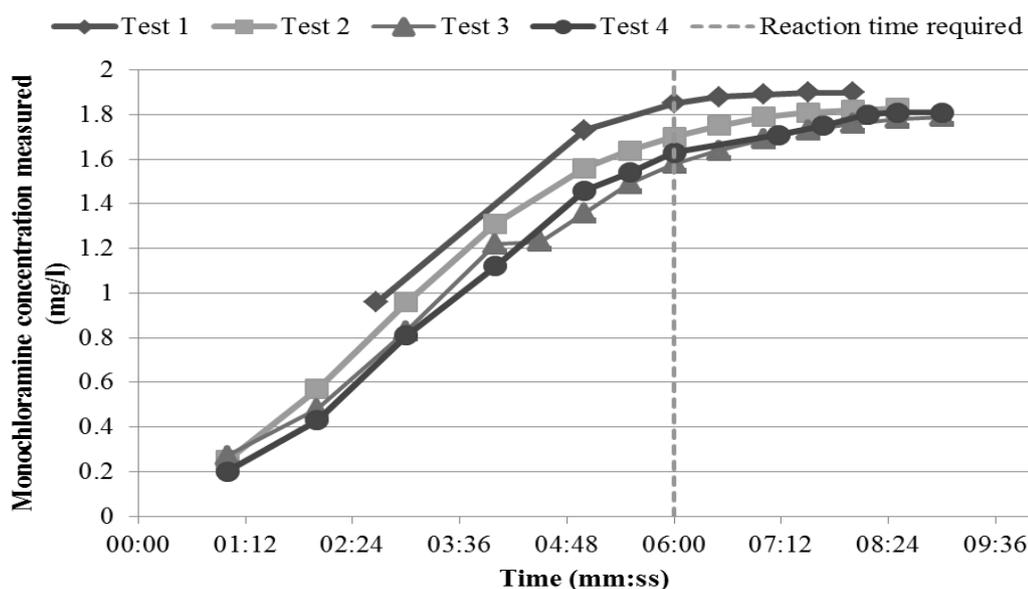

Figure 3:   *Monochloramine residual measurements at different reaction times*

From these results, it is clear that the reaction time is critical. After the specified reaction time, the change in measured concentration diminished over time. Measurements taken one minute before the specified reaction time were approximately 10% too low. However, measurements one minute over the specified reaction time were approximately 5% too high, which was still within the margin of error for the test. Therefore, if the measurement was not taken exactly at the specified reaction time, it was better to measure the monochloramine concentration after the reaction time was completed and not before.

3.0   CONCLUSION

Previously, the method for verifying that the chloramine disinfection plants were operating as expected was through free and total chlorine residual measurements. Through the investigation work of this project it became apparent that there were several issues with only using this type of monitoring, and that other superior methods were available. Due to the interferences in the DPD free chlorine residual measurements, the DPD method was deemed unreliable. To overcome these issues, the best method for determining the monochloramine concentration and free ammonia concentration in the field was found to be the indophenol (Monochlor F) method. Despite identifying some practical issues in measuring the monochloramine residual, these were able to be understood and dealt with, so that the indophenol (Monochlor F) method has greatly improved the monitoring of operational performance.

Although some refining of the testing procedure was required, implementing monochloramine test kits to measure monochloramine residuals has enabled a simple and relatively fast method of verifying that the chloramine disinfection plants are operating as expected. They have also enabled the ability to optimise the ammonia and chlorine dosing to produce monochloramine more efficiently. Furthermore, having the ability to routinely monitor the monochloramine residual has enabled limits for monochloramine residuals leaving the treatment plant to be determined and incorporated into the plant's monitoring and process response plans.

4.0   ACKNOWLEDGEMENTS

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