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STRATEGIES OF USING ONLINE ANALYZER FOR WATER CHLORAMINATION PROCESS MONITORING AND CONTROL

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INTRODUCTION

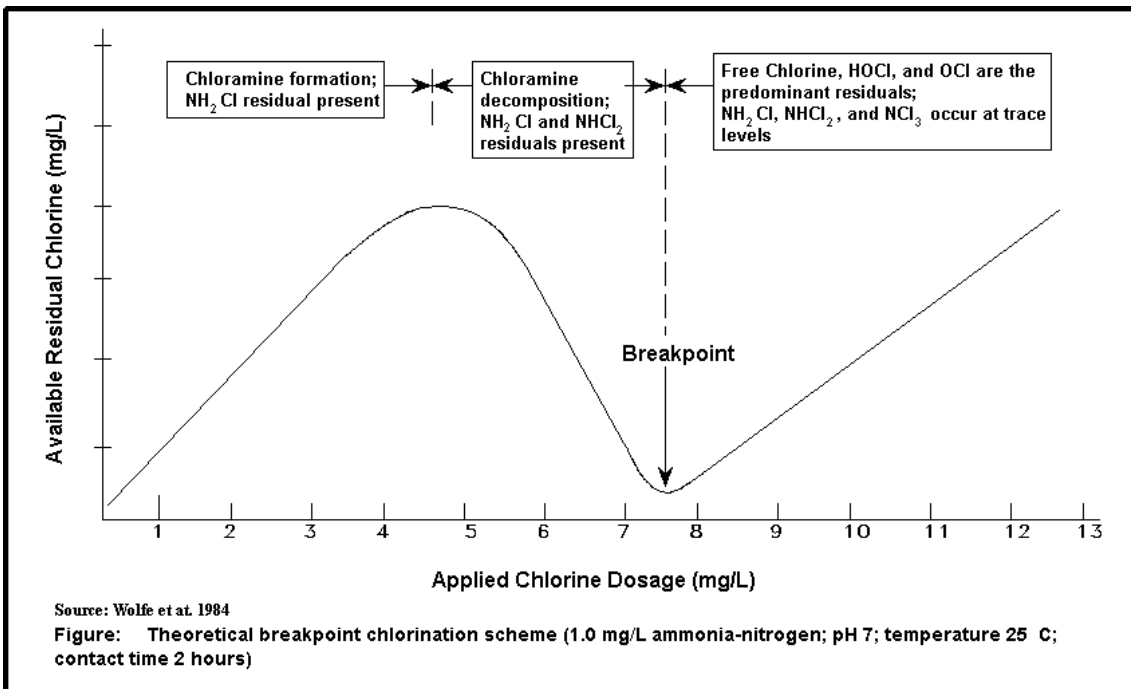
Chlorine has been used for over 100 years as a potable water disinfectant. Chloramine has been used as a disinfectant in the U.S. since the 1930's. In most cases, chloramine is used as a secondary disinfectant while chlorine serves as the primary disinfectant. Use of chloramine has been shown to reduce the formation of trihalomethanes (THMs), while also reducing certain taste and odor problems. Another advantage is that chloramine is more stable, therefore extending disinfectant residual throughout the distribution system. The use of chloramination is increasing in popularity throughout North America, including western Canada. This paper presents some of the fundamentals of chloramination and monitoring strategies in using an online analyzer for chloramination process control. We also present data from a successful on-site demonstration program at one of the City of Toronto Water Treatment Plants.

CHLORAMINATION MONITORING AND CONTROL STRATEGY

Chloramine is formed by mixing chlorine with ammonia. THMs are typically formed from contact between chlorine and organic matter, such as the organic acids found in surface water. THMs formation can be minimized through reduction of organic matter in the treatment process prior to any contact with free chlorine. This is generally accomplished through enhanced coagulation, membrane filtration and other treatment methods employed prior to any primary disinfection. Use of non-chlorine disinfection methods such as UV or ozone for primary disinfection is another strategy to reduce THMs formation. There are three typical methods for the formation of chloramine. (1) *Pre-ammoniation*, where ammonia is fed upstream from the chlorine addition point. This method provides the lowest possible formation of THMs and better taste and odor control, but somewhat less effective disinfection. (2) *Concurrent addition* allows a very short direct contact time for free chlorine with water before reacting with ammonia. This

method optimizes use of free chlorine as a primary disinfectant while reducing the formation of THMs. (3) *Post-ammoniation*, where ammonia is fed downstream from the chlorine addition point. This method provides a substantial contact period for free chlorine with water prior to formation of chloramine. This achieves maximum disinfection but may also maximize THM formation.

Control of formation chemistry is difficult. The reason is that the chlorine to ammonia reaction is not a simple 1 to 1 combination. As the Cl_2 to N ratio increases, the combined species transform from monochloramine to dichloramine to trichloramine and finally to free chlorine and nitrogen gas. Monochloramine is the preferred species of disinfectant, while dichloramine and trichloramine, which create serious taste and odor problems, are undesired forms. As Cl_2 to N ratio decreases, there is extra free ammonia left in the water and it eventually enters into the distribution system (because there is not enough chlorine to react with it). See a typical Break Point Curve below.



Free ammonia in the distribution system can cause many problems, such as nitrification, algae growth, DO deficiency and corrosion control, etc. Maintaining appropriate chlorine to ammonia ratio is an unavoidable challenge to every chloramination water treatment plant.

Three online chloramination monitoring and control strategies are summarized below:

1. Chlorine to Ammonia Nitrogen Ratio Control

This is often referred to as “Ratio Control”. In this method, the chlorine to nitrogen ratio is controlled at or below 5:1. Many water treatment plants try to maintain the ratio between 3:1 and 5:1 in the hope that the predominant chlorine species produced is

monochloramine. The problem of controlling in this way occurs when the applied ratio increases over 5:1. At this point ($\text{Cl}_2 : \text{N} = 5:1$), increasing chlorine dosage results in a decrease of $\text{Cl}_2 : \text{N}$ ratio. This is because the dichloramine and trichloramine, which form at a ratio of greater than 5:1, are not considered to be effective disinfection chlorine species. Other factors may change the actual result (ratio) from the desired ratio. These factors include the metering pump's accuracy and purity of chemicals (solutions) used. Without online monitoring, it is difficult to know where the current chloramination operation point is. In the case of ratio control, the online analyzer can often be used for the purpose of real time monitoring and real time control. A synchronized signal can be used by the operator for adjusting the ratio appropriately. The same signal can also be used for pacing the chemical pump through the plant SCADA system.

2. Free Ammonia Residual Control

Another popular control strategy maintains a very small (at the ppb level) free ammonia concentration to ensure that monochloramine is the predominant species. This method can also be explained as to operate at left, but very close to the top of the Break Point Curve. If the free ammonia concentration is kept very low, the potential of nitrifying bacteria developing in the distribution system is minimized. However, in practicality, the control of free ammonia at the low ppb level is difficult. Using an online analyzer is essential for this type of control strategy. To operate using the residual control strategy, the free ammonia concentration must be set as low as possible to avoid nitrification, while this low level must be far enough above the analyzer detection limit to ensure adequate analysis resolution above and below the set point. A low free ammonia detection limit at 0.02 mg/l is critical for success in minimizing distribution nitrification. This requires an on-line ammonia analyzer capable of rapid low-level free ammonia analysis. Many online ammonia analyzers cannot detect free ammonia at the necessary low concentration. A ChemScan Model UV-2150/S chloramination analyzer can detect down to 0.02 mg/l.

3. Peak Point™ Chloramination Monitoring & Control

Recently, a new approach has been developed by ASA/ChemScan called Peak Point™ Control. This strategy maximizes the development of monochloramine while simultaneously minimizing the free ammonia and dichloramine concentrations. Peak Point™ relies on the observation that when free ammonia is present, the ammonia is being overfed relative to chlorine and when dichloramine is present the ammonia is being underfed relative to chlorine and that under normal treatment conditions these two conditions cannot coexist. A single control signal is created by combining the free ammonia and dichloramine concentrations that is negative when the ammonia is under fed, positive when the ammonia is overfed and at or near zero when the both free ammonia and dichloramine are minimized. The signal is scaled as ppm ammonia to directly represent the amount of ammonia feed change required. This patented control and monitoring strategy is available on ChemScan Analyzers and is possible because of the unique ability of this analyzer to detect all of the necessary control parameters.

AN ON-SITE CHLORAMINATION MONITORING & CONTROL DEMO

The ChemScan Model UV-2150/S on-line process analyzer is manufactured by Applied Spectrometry Associates, Inc. It is designed for the purpose of chloramination process monitoring and control. It is capable of monitoring multiple parameters and multiple sample streams in one centralized analyzer. Many chloramination water treatment plants have had successful experience for either ratio control or residual control with this analyzer. The four parameters offered are free ammonia, total ammonia, monochloramine and total chlorine. Output signals for each parameter are sent from the analyzer to the plant SCADA or other type of central control system, where control decisions are made based on the ammonia to chlorine ratio or other type of control strategy used.

A UV-2150/S was installed at the F. J. Horgan Water Treatment Plant, City of Toronto, for an evaluation test from mid August 2006 to mid Oct 2006. All four chloramination parameters were monitored at the treated water suction channel (after ammonia addition and mixing). The purpose of the demonstration was to demonstrate the reliability of the instrument and to evaluate the maintenance requirements. The goal is to eventually use an on-line multiple-parameter analyzer for chloramination process control and assess the performance of this analyzer for the purpose of process control.

Stable Performance

Charts 2 - 4 show the ChemScan values along with those from the laboratory titration method. Each time a titration sample was collected, the time was recorded. These results were compared with on-line data read from ChemScan at the same time. This procedure is called "Split Sample". Several split samples were prepared using water from the sampling site. One set of samples was assayed by the laboratory titration method and the other set run on the ChemScan. Based on these comparison samples, the internal Calibration File in the ChemScan was adjusted so that the ChemScan values agree with the reference (titration) method. The charts show agreement of the ChemScan values (after initial adjustment) with the laboratory titration values over a three-week period, with no further adjustment of the ChemScan calibration. If it is necessary, the calibration of the ChemScan can be further adjusted by using the Calibration Adjustment feature that can be accessed from the front panel of the instrument. This further adjustment is only rarely required.

There were no split samples for free chlorine available during the period of October 5 to October 11 (Chart 2). But they are available during the rest of the trial (Charts 3 and 4).

Chart 2
Comparison of ChemScan Data with Lab Titration
10-05-06 to 10-11-06

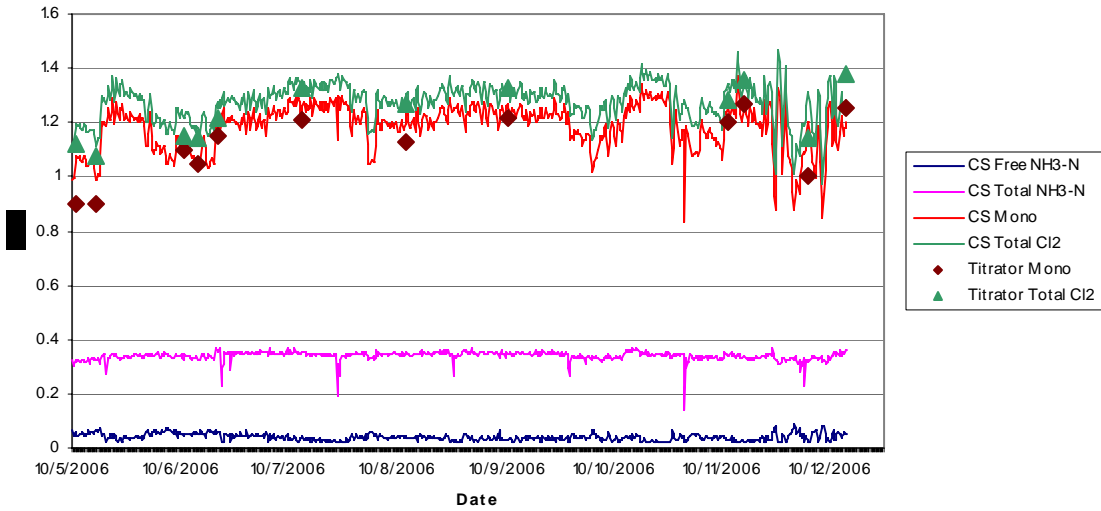


Chart 3
Comparison of ChemScan Data with Lab Titration
10-12-06 to 10-19-06

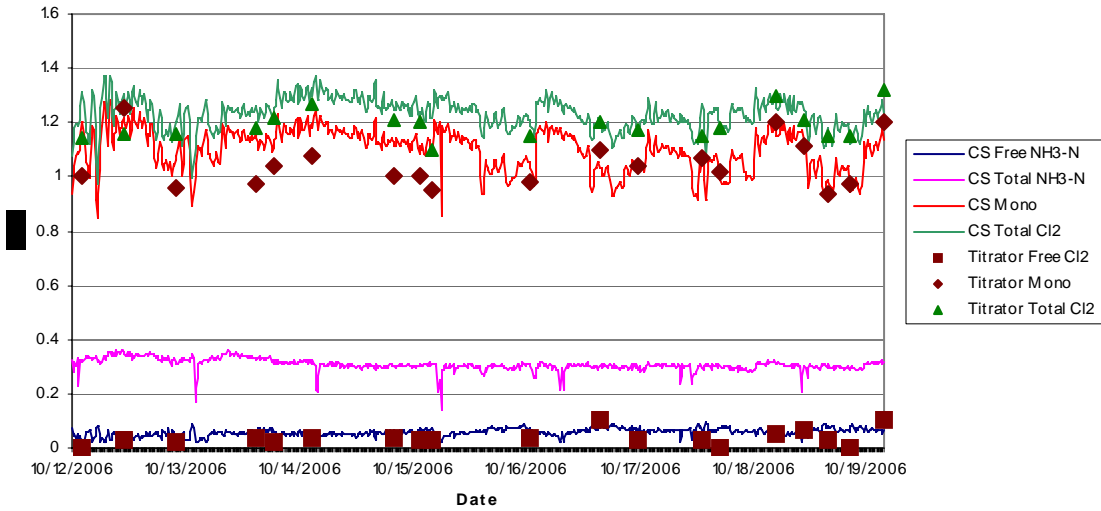
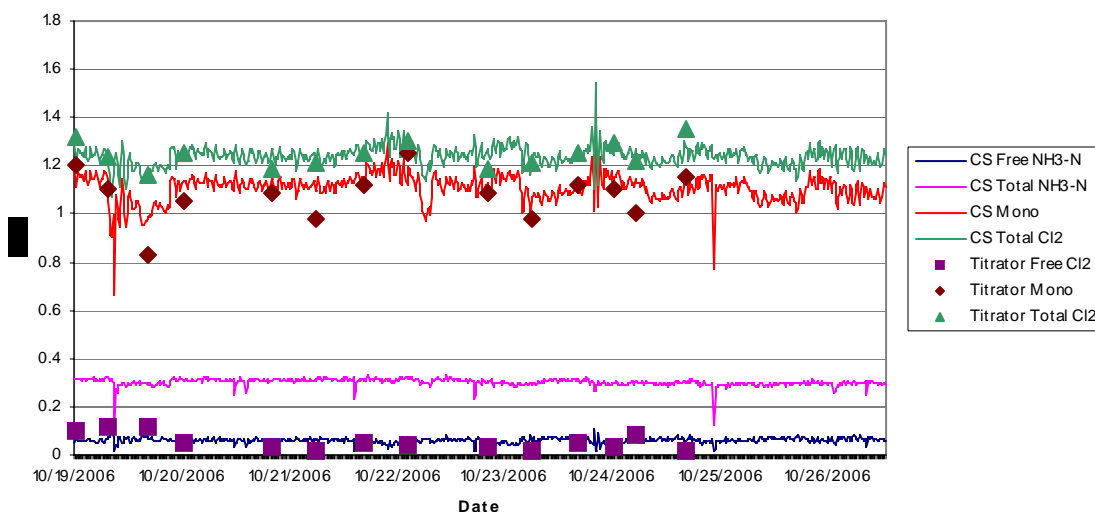


Chart 4
Comparison of ChemScan Data with Lab Titration
10-20-06 to 10-27-06



Observations on the Recorded Data

Total Chlorine

ChemScan readings consistently agree with the results from the laboratory titration method within approximately ± 0.05 mg/l range. Under normal operating conditions, calibration adjustment is suggested if the difference is greater than 0.1 mg/l.

Mono-Chloramine

Generally, the ChemScan readings agree well with the results from the laboratory titration method. There are two days when the laboratory titration results are about 0.1 mg/l lower than the ChemScan results, although the difference does seem to disappear after a few days. No calibration adjustments were made on the ChemScan during this time, so it is possible that the titration process or sample age caused these differences. Mono-chloramine values are consistently 0.1 to 0.2 mg/l lower than total chlorine values, and this indicates good control of the chlorine to ammonia ratio at the plant, with minimal formation of di- and tri-chloramine.

Free Ammonia

It is important in the chloramination process to keep free ammonia from entering the distribution system. There were no free ammonia test results from the laboratory, so we cannot make any comparisons. However, the ChemScan readings for this parameter show a good stable pattern. Free ammonia values are constantly below 0.05 mg/l, which indicates good control of the chloramination ratio and very little free ammonia “leak” to the distribution system. However, free ammonia at the finished water location should be controlled as close to zero as possible. This concept can be explained by the “Break-Point Chlorination Curve.” For optimal control, the plant should be operated as close to the peak of the curve as possible. At this point, free ammonia is close to zero

and di-chloramine will be close to zero also. If the plant is operated on the left side of the “peak”, there will be free ammonia left in the water as it enters the distribution system. Controlling free ammonia near zero is one of the key control objectives. However, because free ammonia is also zero on the right side of the “peak” where di-chloramine forms, it is not the only key parameter.

The most common practice for optimizing chloramination is referred to as the Ratio Control strategy, in which both free ammonia and di-chloramine are monitored. Another method being used in a few plants is called the Residual Control strategy, in which the plant operates (1) on left side of the peak of the break-point curve, to ensure no formation of di-chloramine; and (2) as close to the peak of the curve as possible, to ensure minimum free ammonia entering the distribution system. Therefore, a low detection range for free ammonia is critical for the residual control strategy. The detection range for free ammonia using the ChemScan is 0.02 – 1.00 mg/l. Some plants using the residual control strategy have taken advantage of this low detection range and successfully set up their protocol to adjust chemical feed when free ammonia is higher than 0.05 mg/l.

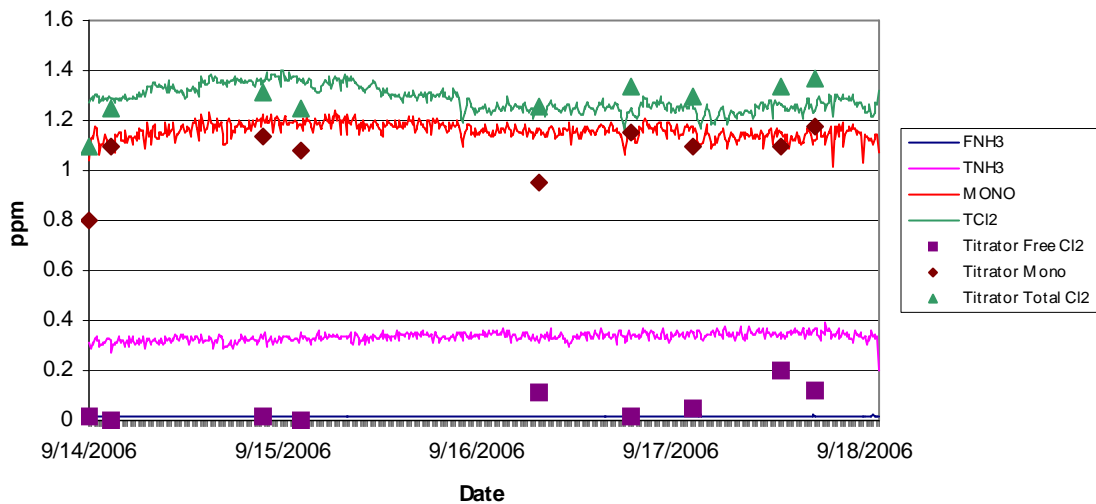
Total Ammonia

Again, we have no total ammonia test data from the Horgan laboratory, so we cannot make any comparisons. However, the readings on the ChemScan for this parameter are quite stable.

Discussion

Process Control using the Analyzer Data

Chart 5
Comparison of ChemScan Data with Lab Titration
09-14-06 to 09-18-06



The analyzer gave an early indication of an ammonia feed control problem. After losing ammonia feed early in September, it was reintroduced on September 12th. Shortly after

ammonia was added, the analyzer gave an indication the ammonia was being underfed resulting a ratio of chlorine to ammonia greater than 5:1. See Chart 5. This was evident in two ways: (1) the free ammonia was constantly at the detection limit of 0.02 mg/l, and (2) the difference between the total chlorine and monochloramine was greater than 0.1 mg/L indicating the formation of dichloramine. It can be noted that during other periods of the trial, the difference is below 0.1 mg/l. An optimized control target is to operate with this value as close to zero as possible. This was verified in the operator titration log sheet as an occasional presence of free chlorine and a consistent difference between the total and mono chloramine greater than 0.1 mg/L.

Calibration of the ChemScan

Initial calibration was not performed during start up. However, at first the slope and offset were adjusted a few times to make the ChemScan agree with another online analyzer. Finally, agreement with the plant was reached to calibrate the ChemScan using only laboratory titration samples. Once this was done, the results showed a very good correlation and no further calibration was necessary.

The normal procedure for ChemScan calibration is that the ChemScan is calibrated against laboratory data once at startup by factory personnel to assure agreement between the analyzer and the on-site laboratory. After initial calibration, the ChemScan data should agree well with laboratory values. Only occasional (once every few months) split comparison samples are needed to check the agreement with the laboratory values. Using simple slope and offset adjustments should be sufficient to maintain agreement. No extensive recalibration is needed. The procedure of performing the adjustment can be found in the ChemScan O&M manual.

Reliability and Maintenance

ChemScan analyzers use daily automatic analysis of a zero standard to maintain a stable optical baseline. An optical analyzer such as the ChemScan uses a beam of light for analysis and therefore has no contact between a "sensor" and the sample. The automatic zeroing procedure used by the analyzer maintains optical stability, subtracts out any effects of deposits on cell windows and triggers automatic cleaning if the deposits exceed allowable set points. The reagent-assisted methods used by the ChemScan for analysis of the sample always subtract the full spectrum of a sample blank from the full spectrum of the reacted sample, thus removing background chemistry variations from the resulting spectrum prior to the analysis calculations. All reagent and cleaning solutions used in the ChemScan analyzer are commercially available. ChemScan also provides the chemical composition of these reagents. The chemical cost for the ChemScan chloramination analyzer is less than \$50 per month. There is no need to purchase proprietary reagents.

Operator maintenance is limited to topping off of reagents, zero standard and cleaning solution, as well as taking an occasional comparison sample. Replacement of solutions is typically required only once a month, so the amount of work involved is only a few minutes per month.

Demonstration Project Summary

- Values from the analyzer agree well with those from the laboratory titration method.
- Analyzer can be easily calibrated using values from the laboratory titration method.
- Analyzer can be used to coordinate with plant SCADA for chloramination control.
- Analyzer requires little maintenance during operation.

BENEFITS OF USING AN ONLINE ANALYZER FOR CHLORAMINATION PROCESS CONTROL

Control of chloramination chemistry is always a challenging task. An appropriate online analyzer can definitely help in this process, by providing a rapid automatic analysis of the key chloramination control parameters including free ammonia, total ammonia, monochloramine and total chlorine. There are many small or midsized surface water treatment plants using chloramination throughout North America. Some of them still operate based on grab samples. Experience shows that several water quality problems may occur during run off season, when run off carries a large amount of animal waste and organic matter into surface water. Groundwater may also be affected by fertilizers and other contaminants, creating a high background ammonia concentration in the water. When problems such as this happen, a real-time analysis allows the plant operator to adjust the water chemistry promptly. The same adjustment process can be accomplished automatically using a plant SCADA. A daily grab sample is just not sufficient for proper water chemistry control.

Chloramination process optimization is even more challenging. To operate at the right chlorine to ammonia nitrogen ratio, the process needs to be constantly monitored with the *right parameters*. No matter which control strategy is adopted (Ratio Control or Residual Control or Peak PointTM control), a single parameter may not be adequate. For example, the same monochloramine reading can be obtained at different chlorine to ammonia ratios. The best way is to use multiple parameters (such as free ammonia, total ammonia, monochloramine and total chlorine) to detect what the real ratios and concentrations are and to adjust chemical addition accordingly.

CONCLUSION

Even though Chloramination of drinking water has been used since the 1930s, the usage has greatly increased over the past few years due to increasing concerns over the formation of disinfection byproducts such as trihalomethanes (THMs) when free chlorine is used. The Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR) posted by USEPA has been finalized on December 2005. It set the maximum contaminant level for TTHM at 80 ppb and HAA5 for 60 ppb. The implementation of this chemistry can be a challenge for plants currently dosing only chlorine and an effective control strategy must be developed. There are several strategies that can be used to effectively control chloramination chemistry in potable water, including Ratio control, Residual control and Peak PointTM control. These strategies can be most effectively implemented using an on-line water chemistry analyzer that can detect the key water chemistry parameters: free ammonia, total ammonia, monochloramine and total chlorine. One analyzer capable of performing these analyses is the ChemScan UV-2150/S. This analyzer was specifically developed for chloramination applications in the 1990's and

has been installed in many water treatment plants across North America. It was most recently tested successfully at the F.J. Horgan Water Treatment Plant in City of Toronto.

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