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PROCESS ANALYZERS

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ChemScan® Application Summary #154 Peak Point™ Chloramination Control

Over the past few years the EPA has tightened the regulations on suspected cancer causing disinfection byproducts in the nations drinking water. These byproducts result from the reaction of naturally occurring organic material (such as decaying plants) with chlorine. Water treatment plants have implemented better Natural Organic Material (NOM) removal and some began adding Ammonia to combine with chlorine following the primary disinfection process. By adding Ammonia to chlorinated water, the two chemicals combine to form a less reactive disinfectant residual in the water distribution system.

The need has been growing for a reliable on-line analyzer to help water treatment plants control this rather finicky chemistry. Some plants have been chloraminating for many years and have developed their own techniques for measurement and control. However, the new EPA regulations have encouraged water utilities to convert to chloramination that have not even considered it before. There is currently no standard operating procedure regarding the monitoring and control for the addition of ammonia, although the regulations do require regular measurement of chloramine in the distribution system. Each plant (or their consulting engineer) decides how they will measure the chemistry and control the process.

The reason this chemistry is so difficult to control is that the chlorine/ammonia reaction is not a simple 1 to 1 combination. As the CL₂ to N ratio increases, the combined species transform from monochloramine to dichloramine to trichloramine and finally to free CL and Nitrogen gas. Figure 1 depicts the effect on total CL₂ as a function of CL₂ to N ratio. The preferred species of chloramine in water treatment is monochloramine. Monochloramine is preferred because it has an increased disinfecting power compared to other forms of chloramine and because di- and tri-chloramines exhibit a pungent taste and odor. A number of other variables affect the control including chlorine demand of the water, pH, temperature and contact time. One typical solution to controlling the chloramine species is to simply overfeed the ammonia to keep the CL₂:N ratio down at 3:1 to 4:1. However, the long term effect of this is the development of nitrifying bacteria in the distribution system, which requires shocking the system with free chlorine to reduce the bacteria counts.

In most cases, the chlorine and ammonia is applied to achieve a total chlorine level. Then the ammonia is tuned to maximize the monochloramine while minimizing the free ammonia.

Two control strategies have emerged as the preferred methods.

CL₂:N Ratio Control:

If the chlorine to nitrogen ratio is at or below 5:1 the predominant chlorine species will be monochloramine. The problem of controlling this way is the fact that as the applied ratio increases over 5:1, both the measured total chlorine and total ammonia drastically decrease, and not at the same rate. One current on-line analyzer being marketed for this analysis by a major company (not ASA/ChemScan) uses a measurement of the monochloramine to calculate the total ammonia. Figure 2 shows that the monochloramine value actually decreases as the CL₂:N ratio increases over 5:1. This can lead to a false ratio calculation if the ratio increases over 5:1, creating incorrect control decisions.

Free NH₃ Control:

The other popular control strategy uses a very small (ppb) free ammonia concentration to ensure that monochloramine is the predominant species. 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 range is difficult because of other variables affecting feed rates and chlorine levels. Many on-line ammonia analyzers cannot detect free ammonia at the necessary low concentration (ChemScan can detect down to 0.01 mg/l). In these cases, di- or tri-chloramines can be created. To ensure this does not occur, the free ammonia concentration must be set high enough above the analyzer detection limit to ensure adequate analysis resolution above and below the set point. This requires an on-line ammonia analyzer capable of rapid low level free ammonia analysis.

A New, Simplified Control Strategy: Peak Point Chloramination Monitoring and Control

The ideal monitoring and control strategy would provide means to produce chloraminated water with as little free ammonia and as little dichloramine as possible. Recognize that when free ammonia is present, the ammonia is being over-fed and when dichloramine is present the ammonia is being under-fed and that these two conditions cannot exist at the same time. Developing a balance between these two conditions provides the best possible control.

The amount of "over feed" of ammonia is simply the amount of free ammonia. Conversely, the amount ammonia combined in dichloramine is the amount ammonia that is under fed. The under fed ammonia concentration can be calculated by simply dividing the dichloramine concentration by 10.

To produce a single ammonia control signal, ammonia combined with dichloramine is subtracted from the free ammonia concentration.

Three conditions can occur:

- 1) The signal is positive: This indicates the amount of overfed ammonia in ppm and the controller should decrease the ammonia feed rate.

- 2) The signal is negative: This indicates the amount of underfed ammonia in ppm and the controller should increase the ammonia feed rate.
- 3) The signal is zero: This is the optimal balance between free ammonia and dichloramine.

Chlorine Specification:

The analysis of combined chlorine can be broken down into the measurement of monochloramine and total chlorine. The difference between these measurements has been defined as the concentration of dichloramine in the sample.

Free Ammonia:

The free ammonia is measured directly using the measurement of additional monochloramine when a small amount of chlorine is added to the sample at an elevated pH.

This is called Peak Point Control, because it will assure that the process is maintained at the peak of the chloramine formation curve, where monochloramine is at the maximum possible concentration, free ammonia is minimized and no dichloramine formation has occurred. An analysis technique has been developed to provide the necessary information to produce this unified signal using a ChemScan UV-2150/S Analyzer. This is a patent pending technique. A single ChemScan analyzer is used to sequentially measure the above three parameters. The single ammonia control signal is then determined by mathematically combining the results.

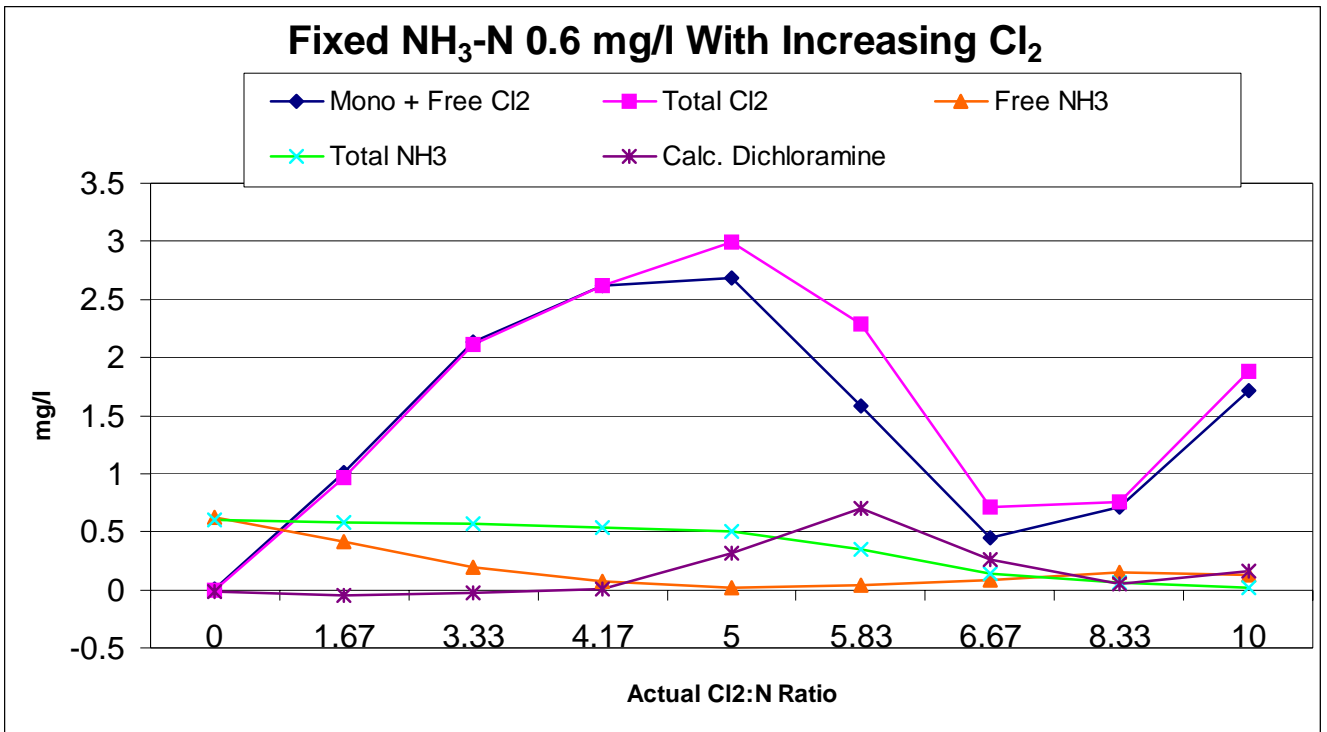


Figure 1. Breakpoint curve: Fixed Ammonia, Concentration vs Chlorine to Ammonia Ratio.

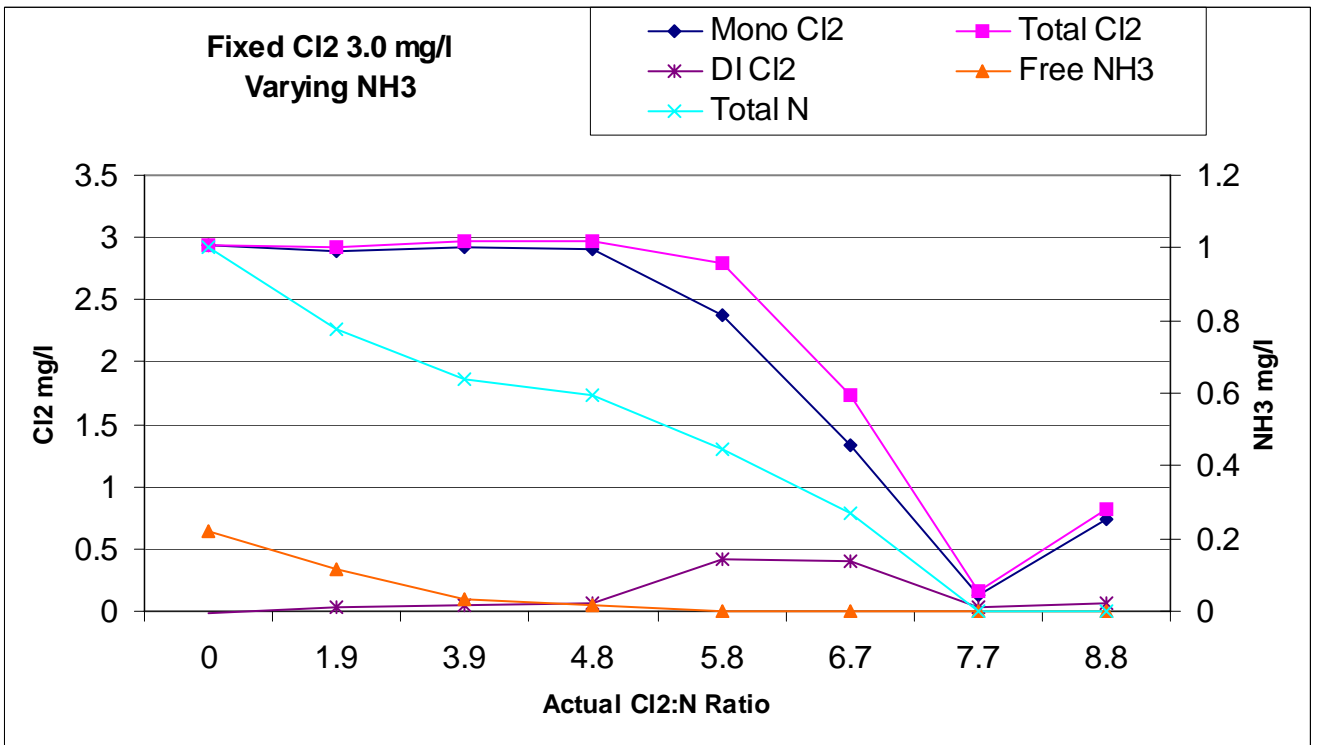


Figure 2. Breakpoint curve: Fixed Chlorine, Concentration vs Chlorine to Ammonia Ratio.

