Application Note 123

Monitoring Chloramination using the APA6000™ Ammonia/Monochloramine Analyzer

Introduction

Chloramination, a process often used for disinfection of drinking water and wastewater, involves mixing chlorine and ammonia to form chloramines. The relative concentrations of both chlorine and ammonia are essential for optimum disinfection. Some reactions between ammonia and chlorine are still being investigated, but in general, if chlorine is added to ammonia at a relatively neutral pH (similar to most municipal applications) a predictable series of reactions will occur.

First, the chlorine will react with free ammonia to form monochloramine. As more chlorine is added, additional monochloramine is made until all the free ammonia is consumed. When all the free ammonia is gone, the chlorine will begin to react with the monochloramine to form dichloramine. This reaction will continue until all the monochloramine is gone. If more chlorine is added, the chlorine will react with the dichloramine to form trichloramine (also called nitrogen trichloride) until all dichloramine has been reacted. This is called breakpoint and no more reactions are possible between the ammonia and chlorine. If more chlorine is added, it will remain as free chlorine in solution.

Each chloramine has a different effect on disinfection and the key to chloramination is to produce the correct chloramine species. Monochloramine is an effective disinfectant, is relatively stable in solution, and is often the preferred disinfectant in drinking water. Dichloramine is also a strong disinfectant but often gives an off taste and odor in drinking water. Trichloramine is unstable in solution and decomposes quickly.

The current analysis techniques available to monitor chloramination typically rely on the measurement of total chlorine along with the measurement of free ammonia. These two analyses are typically performed independently using two different process analyzers. The measure of total chlorine provides a good indication of chlorine level, but provides no detail as to which species of chlorine is being produced. In some cases, a second chlorine analyzer is added to measure free chlorine (which occurs at breakpoint). Doing so provides an indication of extreme chlorine overfeed condition but does not prevent or predict the incorrect ratios of ammonia and chlorine that result in the production of dichloramines and trichloramines.

An extreme chlorine overfeed condition results in poor disinfection despite a positive chlorine residual. In addition, many total chlorine tests are affected by interferences, resulting in a false high reading. The addition of a free ammonia analyzer lets the operator know that ammonia is being overfed but does not always give reliable results near the ammonia lower limit of detection. When the chloramination process is in control, a low ammonia concentration is the goal and the analyzer must monitor near the limit of detection. In many ion selective electrode-based ammonia analyzers, these low readings are difficult to reliably achieve because of interferences in the sample stream.

In summary, adequately monitoring chloramination with current technology requires three separate analyzers and the end result is still better suited to identify out-of-control conditions than to fine tune and optimize chloramination.

The APA6000™ Ammonia/Monochloramine Analyzer was developed based on input from customers performing chloramination. The analyzer addresses the process analyzer weaknesses described above to provide an accurate indication of both the monochloramine concentration and the ammonia concentration. The focus is on an analyzer capable of optimizing chloramination by specifically monitoring monochloramine. It does not detect dichloramine, trichloramine, or free chlorine so instead of only catching upset conditions, it also can focus on controlling and optimizing typical operating conditions.

In addition, the analyzer monitors ammonia levels by determining a ‘total ammonia’ value. Total ammonia is defined as the concentration of monochloramine plus free ammonia. By monitoring monochloramine and total ammonia, the analyzer is capable of calculating the free ammonia as well as the chlorine to nitrogen ratio. This allows control and optimization of chloramination using a single analyzer.

Figure 1 shows the response for total chlorine, monochloramine, total ammonia, and free ammonia when ammonia feed is constant and the chlorine feed is changing. All results are reported in mg/L as N. This figure is separated into three regions.

Region #1 is the operating region for most chloramination systems. In this region, as chlorine feed increases, the chlorine reacts with ammonia to form monochloramine. This results in an increase in monochloramine and a decrease in free ammonia. The desired set point is often the point at which free ammonia reaches zero. This is also the maximum point for monochloramine.

Feeding more chlorine results in operating in region #2. In this region, dichloramine and trichloramine (nitrogen trichloride) are formed. Monochloramine decreases with increased chlorine feed and no free ammonia is present. Operating in region #2 is not desired in most chloramination systems since it requires more chlorine, provides less disinfection, and often results in taste and odor problems.

Finally, in region #3, chloramination is no longer being performed. All nitrogen species have been consumed by chlorine, leaving free chlorine as the disinfectant.

The current approach to monitoring chloramination using a total chlorine analyzer and a free ammonia analyzer provides information, but has some practical difficulty. The total chlorine value can be used to control chlorine feed. However, the same chlorine value can be obtained in region #1, #2, and #3. So this analyzer alone does not provide enough information for control. If ammonia feed changes suddenly, the chlorine feed could be adjusted to maintain a given total chlorine value in region #2, or #3. The practical limitation of a total chlorine measure is that it responds equally to all chloramines and free chlorine, yet these different species do not provide the same disinfection properties. Speciation is important.

The goal in chloramination is to maximize the reaction of ammonia and chlorine to form monochloramine. When monochloramine production is maximized, free ammonia is minimized, potentially at or very close to zero. The addition of a free ammonia analyzer adds more control to the chloramination process by monitoring and controlling ammonia feed. Unfortunately, using a free ammonia value as the basis of control is flawed because this analysis requires the presence of a measurable concentration of ammonia. Because of this, the chloramination process is limited by the detection limits of an analyzer. If a measurable concentration of ammonia is present, monochloramine production is not maximized.

Operating at or near the detection limits of any analyzer offers challenges. It is difficult to obtain reliable readings near the detection limit because of factors such as interferences, drift, and changes in ambient temperature. Operating at higher levels of free ammonia does not allow process optimization.

The APA6000 Ammonia/Monochloramine Analyzer uses a single instrument to address the shortcomings of independent chlorine and ammonia analyzers. Monochloramine is measured instead of total chlorine, allowing the chlorine feed to be controlled using a monochloramine set point.

Because monochloramine is also produced in region #2, monitoring only monochloramine could result in the process operating in region #2. The APA6000 warns the operator of this condition by outputting dashed lines for the ammonia values. So, chlorine feed can be optimized to operate in region #1 based on monochloramine. The ammonia feed can also be optimized based on the total ammonia value. Total ammonia is a good indication of ammonia feed as opposed to the remaining free ammonia. Figure 1 assumes a constant ammonia feed and the total ammonia value indeed remains constant throughout all of region #1. Total ammonia can be used to control ammonia feed. If the conditions change and the process extends into region #2, the total ammonia will begin to decrease as dichloramines are formed. However, this condition, as mentioned above, is indicated by dashed lines for the ammonia species. So, in a single analyzer, both chlorine and ammonia feeds can be controlled and the process optimized. The analyzer indicates when the process goes out of control, yet it is designed to fine tune proper operation.

Figure 1 **Monitoring Chloramination using an APA6000 Ammonia/Monochloramine Analyzer—Chlorine feed Changing/Ammonia Feed Constant**

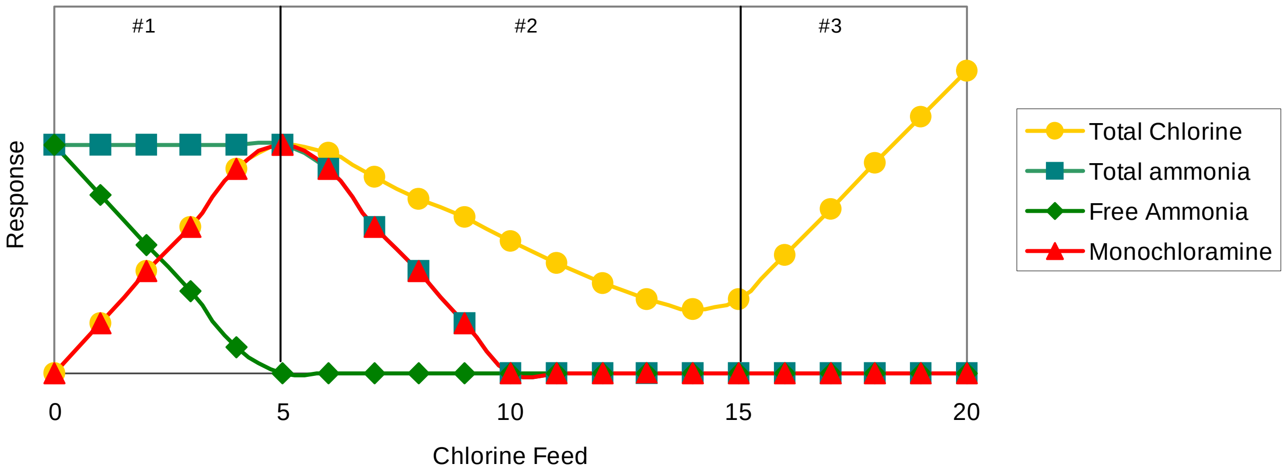
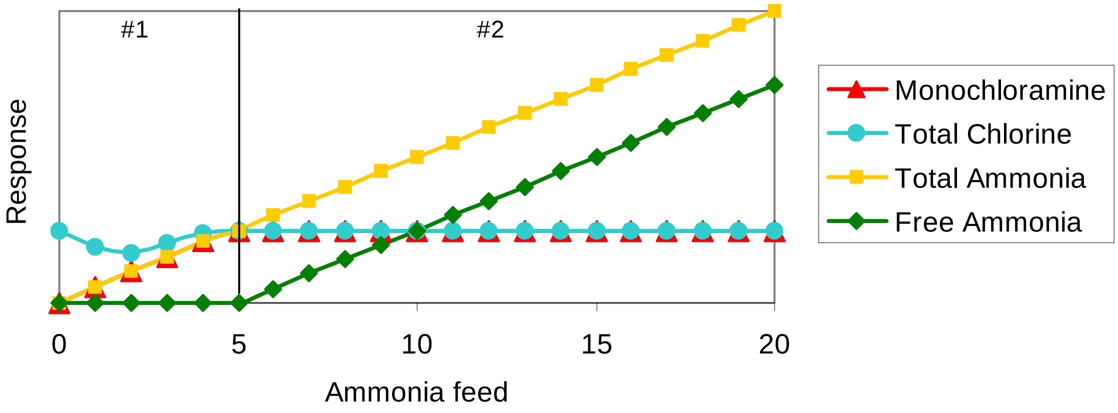


Figure 2 shows the response for total chlorine, monochloramine, total ammonia, and free ammonia when the chlorine feed is constant and the ammonia feed is changing. The results are all reported in units of mg/L as N. This figure is separated into two regions. Region #1 indicates low ammonia feed which would result in the formation of dichloramines and trichloramines. Region #2 is the operating region for most chloramination systems. The setpoint for control would likely be at the transition from region #1 to region #2. At this point the monochloramine reaches a maximum while the free ammonia is still zero. Region #2 indicates adequate ammonia feed and monochloramine values do not change in this region. Total chlorine values are also constant. This figure clearly shows the direct relationship of the ammonia feed to the total ammonia value. Current methods monitor for free ammonia and base ammonia feed rates on the reported ammonia values. Since free ammonia is not present until after the optimum setpoint, when ammonia is being underfed, monitoring for free ammonia provides no information. Monitoring instead for total ammonia will provide a value to base ammonia feed.

Figure 2 **Monitoring Chloramination using an APA6000 Ammonia/Monochloramine Analyzer—Ammonia feed Changing/Chlorine Feed Constant**



Performing a straight free ammonia measurement on ISE analyzers often fails to provide accurate readings at low levels (such as those seen in the control region) because the values are very close to the lower limit of detection for the analyzer. Ideally, the free ammonia values of an ISE analyzer and those calculated by the APA6000 will be identical. In reality, free ammonia measurements made by an ISE near the limit of detection can exhibit a slow response, be affected by other interferences, or show electrode drift.

The APA6000 ammonia/monochloramine analyzer offers the ability to control and optimize chloramination. The ammonia feed can be controlled based on the total ammonia value and the chlorine feed can be controlled based on the monochloramine value. By setting the total ammonia control point slightly higher than the monochloramine control point, chloramination can be optimized using a single analyzer.

Operation of the APA6000™ Ammonia/Monochloramine Analyzer

The APA6000™ analyzer uses a colorimetric chemistry to measure total ammonia and monochloramine. The chemistry is a modified Phenate approach optimized for stability, dynamic range, and fast reaction time. The same chemistry is used to monitor both total ammonia and monochloramine.

In the measure of monochloramine, a buffer and indicator are added step-wise to the sample. The buffer and indicator form a green color when monochloramine is present. The color increases in intensity with increasing monochloramine. A short reaction time is allowed and the mixture of sample and reagents flow through an LED-based single wavelength colorimeter. The concentration is determined based on the absorbance at 650 nm.

Total ammonia is determined in much the same way. However, prior to adding the buffer and indicator, an excess of hypochlorite is added at a high pH to convert any free ammonia present in the sample to monochloramine. The remainder of the analysis is identical to the monochloramine method. The total ammonia result indicates the combination of any monochloramine initially present in the sample plus any monochloramine formed from free ammonia. Maintaining the proper pH prevents the formation of dichloramine even when excess chlorine is present.

The monochloramine analysis and the total ammonia analysis cycle alternately. Following each cycle, the free ammonia and the chlorine to nitrogen ratio is calculated and reported.

Free ammonia and the chlorine to nitrogen ratio are calculated from the total ammonia and monochloramine values. If the total ammonia and monochloramine values are equal (indicating no free ammonia is present) the analyzer defaults to dashed lines for both the total ammonia and free ammonia values, indicating a potential overfeed of chlorine. (Ask your Hach sales or service personnel to disable this default condition if desired.) As noted in Figure 1, once the monochloramine and total ammonia values are equal, they will remain equal with increasing chlorine feed. Therefore, if a monochloramine value is present, but dashed lines are indicated for total and free ammonia, it can be assumed the total ammonia value is equal to the monochloramine value and the free ammonia content is zero.

The method used in the APA6000 is a patented technique called Carrierless Sequential Injection Analysis (CSIA). This technique mixes sample and reagents in small volumes in a very reproducible way for faster analysis. The method relies on a multi-port valve to select either samples, reagents, or standards and to direct the fluid to the mixing chamber or detector. The fluid is moved by a high precision burette. A small mixing chamber and a single wavelength LED-based colorimeter complete the modules found in an APA6000. Temperature control is used to ensure accurate results and the detector line is maintained under a slight back pressure to minimize outgassing.

The analyzer auto-calibrates using ammonia standards. It treats these known concentration standards the same as a sample. Each of the two standards provided with the analyzer is measured for total ammonia. Thus all the ammonia in the standard is converted to monochloramine. The absorbance is related to the concentration through these known standards which accounts for any slight changes in the reagents over time. To assure the reagents are still operational, a third standard is made by the analyzer. This third standard is an equal mixture of the two provided standards. The analyzer determines if the absorbance of the third standard is within the proper range. If not, it warns of the potential degradation of a reagent. The reagent most susceptible to degradation is Reagent 3 (the hypochlorite reagent) because it is highly light sensitive. Typical shelf life for Reagent 3 is six months. Failure to protect it from light may lead to faster degradation.

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