Chloramination Application Note

Introduction
Chloramination disinfection is the practice of forming inorganic chloramines in water to reduce microbial concentrations to within acceptable limits. The chloramines – monochloramine (NH₂Cl), dichloramine (NCl₂), and nitrogen trichloride (NCl₃) – form when chlorine and ammonia are combined in water. Traditionally, treated wastewater, which contains ammonia, is disinfected by the addition of chlorine. In recent years, many drinking water facilities have converted to chloramination to disinfect potable water. Roughly 20% of all drinking water facilities in the United States now use chloramines as the residual disinfectant.

For the chloramination of drinking water, monochloramine is the preferred disinfectant. Formation of dichloramine and nitrogen trichloride is avoided, since more chlorine is consumed and the presence of these chloramines can produce odors or off-tastes.

In treated wastewater, any organic nitrogen compounds present will form organic chloramines during chlorination. Organic chloramines, as a class, are much weaker disinfectants than the inorganic chloramines. Chlorine overfeeds and ineffective mixing can lead to greater production of organic chloramines, thus diminishing the total germicidal activity.

Problems with Conventional Chloramination Control Strategies
There are two traditional methods for controlling the disinfection of water: residual maintenance and oxidation-reduction potential (ORP).

In residual control, analytical measurements are made either manually (e.g., laboratory or field testing) or automatically (e.g., a process analyzer). All of the commonly used methods for residual control are based on iodometric chemistry. Either the inorganic chloramines or the organic chloramines will oxidize iodide (added as a reagent) to the tri-iodide ion:

\[
\text{NH}_2\text{Cl (monochloramine)} + 3\text{I}^- + \text{H}_2\text{O} + \text{H}^+ \rightarrow \\
\text{NH}_2\text{OH} + \text{Cl}^- + \text{I}_3^- \text{ (tri-iodide)}
\]

\[
\text{OrgNH–Cl (organic chloramines)} + 3\text{I}^- + \text{H}^+ \rightarrow \\
\text{OrgNH}_2 \text{ (organic amine)} + \text{Cl}^- + \text{I}_3^-
\]
The resulting tri-iodide ion can be measured either colorimetrically (e.g., DPD method), amperometrically (e.g., amperometric back-titration method), or by direct titration (e.g., vs. thiosulfate reagent). The iodometric methods currently used for residual control are not specific for the preferred disinfectant, monochloramine.

In wastewater chlorination, the presence of organic nitrogen compounds, manganese, and/or nitrite will bias the residual control methods high, thus possibly over-estimating the disinfection efficiency. For drinking water chloramination, the conventional residual control methods do not provide enough information about the break-point chlorination profile. If a 3.0 mg/L result is obtained by the conventional residual methods, the operator cannot be sure whether monochloramine, a mixture of chloramines, or free chlorine is present (see Fig. 1).

**Fig. 1: Break-Point Chlorination Profile**

Recently, ORP has become popular for wastewater disinfection control. ORP is based on the concept that it is the oxidative potential derived from the residual that kills the microorganisms and not the concentration of the residual. In practice, a set-point ORP value (measured in millivolts) is maintained using an ORP controller. As indicated in Fig. 2, ORP can distinguish between pure solutions of monochloramine and dichloramine, but cannot distinguish between monochloramine and organic chloramines at levels typically found in chlorinated wastewater effluents. Hence, as with residual control, the weaker-disinfecting organic chloramines will also be indicated in ORP chlorination control.

**Fig. 2: ORP Profiles**
A Test Method Specific for Inorganic Monochloramine

Hach chemists have developed a method for the specific determination of monochloramine in water. The method is based on the classic indophenol chemistry for determining ammonia. The chemistry has been improved to increase the specificity of the method for inorganic monochloramine in the presence of organic chloramines. In addition, the method was modified to greatly accelerate the color development time and increase the precision of the test.

The new method is available in two ranges: 0 – 4.50 mg/L Cl₂, designed for drinking water and some wastewater chloramination control and a higher range of 0 – 10.0 mg/L Cl₂, which has application for wastewater chlorination control. The lower range test uses just one combined powder reagent (Monochlor F) with test results obtained within 3 minutes at room temperature. The higher range test employs one additional reagent, packaged in a Test ‘N Tube™ (TNT).

The new test has been shown to be specific for monochloramine, without interference from organic or inorganic amines, dichloramines, free chlorine, organic chloramines, nitrites or manganese. Portable systems are available for testing monochloramine residuals at the sampling site. A process analyzer (APA 6000 Ammonia/Monochloramine) for automated chloramination control has been developed based on the improved chemistry.

Practical Applications of Monochloramine Control

A large metropolitan water district on the U.S. West Coast uses the Monochlor F control strategy to maintain effective potable water disinfection and a variant of the chemistry to control and limit free ammonia leaving the plant. Coupled with field testing, this control strategy has enabled the district's facilities to maintain adequate levels of monochloramine throughout their distribution lines while minimizing the potential for nitrification.

One regional wastewater facility receives 80% of its loading from a large meatpacking plant. On occasion, the treatment facility has had difficulty in meeting the requirements of its discharge permit for fecal coliforms, even though conventional testing indicated adequate chlorine residuals in the final effluent. A chlorination study of the treated water indicated that it contained appreciable levels of organic chloramines, which registered in the hourly chlorine testing. Figure 3 illustrates significant difference between the iodometric methods (DPD and Amperometric Titration) and the Monochlor F results along the break-point profile. The Monochlor F test specifically indicates the active disinfectant, monochloramine, without interference from the organic chloramines present.
Conclusions
The new chloramination control strategy, using Monochlor F chemistry, benefits both drinking water and wastewater chloramination disinfection control. It allows drinking water treatment operators to maximize monochloramine without the production of objectionable dichloramine. The method allows wastewater treatment operators to accurately monitor monochloramine without interference from organic chloramines, nitrites, or manganese. Chloramination control monitoring monochloramine can help the wastewater facility to comply with their microbiological permit requirements. It will assist the treatment facilities in controlling excessive chlorine and ammonia feed costs.

Patent pending

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