TECHNICAL APPLICATION BULLETIN

Chloramines

Recognized Treatment Techniques For Meeting Drinking Water Regulations For The Reduction Of Chloramines From Drinking Water Supplies Using Point-of-Use/Point-of-Entry Devices And Systems

PREPARED AND DISTRIBUTED BY THE

Water Quality Association

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Recognized treatment techniques for meeting drinking water regulations for the reduction of chloramines using point-of-use and point-of-entry (POU/POE) devices and systems.

Occurrence & Chemistry

Aqueous chlorine reacts with certain organic materials present in water sources to form trihalomethanes (THMs). Long-term exposure to these harmful byproducts of disinfection has been linked to an increased risk of cancer and infant birth delivery problems. It is estimated that THMs in drinking water are responsible for as many as 2-17 percent of the bladder cancers diagnosed each year in the United States. To protect the public, the U.S. Environmental Protection Agency has established a maximum contaminant level of 0.08 milligrams per liter (mg/L) for THMs. To conform to these regulations, many municipal water supplies have switched to an alternative method of disinfection using chloramination.

Chloramination involves the addition of anhydrous or aqueous ammonia (NH_3) before or after the addition of chlorine (HOCl) to produce monochloramine (NH_2Cl). This reaction is as follows:

$$NH_3 + HOCl = NH_2Cl + H_20$$

Chloramines also form to a lesser extent during conventional chlorine treatment when aqueous chlorine reacts with natural organic nitrogen.

Monochloramine is 200 times less effective as a disinfectant than chlorine, but is an attractive alternative since it does not react as readily with organic materials to form THMs. Many water utilities overcome the decreased efficiency of monochloramine by adding ammonia following the chlorine application. This increases biocidal efficiency, but also increases the risk of THM formation.

The process of chloramination is both pH and concentration dependent. Water pH levels below 7.5 or chlorine to ammonia ratios exceeding 5:1 increase the formation of dichloramine ($NHCl_2$) and nitrogen trichloride (NCl_3). Dichloramine and nitrogen trichloride are undesirable byproducts in that they are less effective disinfectants and may cause greater "swimming pool"-type taste and odor problems when they exceed concentrations of 0.8 mg/L and 0.02 mg/L (respectively). Excessive chlorine levels produce THMs, while excess ammonia increases the potential for nitrification in the distribution system. The U.S. EPA recognizes three analytical methods as acceptable for measuring residual chloramines. These methods are:

- Amperometric Titration (Standard Method 4500-C1 D and ASTM Method D 1253-86)
- DPD Ferrous Titrimetric (Standard Method 4500-C1 F)
- DPD Colorimetric (Standard Method 4500-C1 G)

The average municipal water system maintains residual monochloramine concentrations around 2 mg/L (range: 1.5 mg/L to 2.5 mg/L). Chloramination also has the added benefit of decreasing the formation of biofilms in water supply systems since the residual levels of monochloramine remain relatively constant throughout the system.

Health Effects

Although the use of chloramination has recently increased, it has a long history of safe and effective use in the United States. The City of Denver, Colorado has utilized chloramination since 1918. An extensive risk assessment by the EPA's National Center for Environmental Assessment (NCEA) utilized existing human and animal studies to conclude that human health effects do not appear to be associated with levels of residual chloramines typically found in drinking water. However, a Maximum Residual Disinfectant Level Goal (MRDLG) and a Maimum Residual Disinfectant Level (MRDL) of 4.0 mg/L was established by USEPA as the enforceable maximum safety level for chloramines (measured as chlorine,Cl_2) for public water systems under the Safe Drinking Water Act, and the level below which there is no known or expected risk to health..

Chloramines do pose a risk for hemodialysis patients and fish. Chloramines easily enter the bloodstream through dialysis membranes and the gills of fish. Once in the blood stream, chloramines denature hemoglobin and cause hemolytic anemia. Accidental use of chloramine treated water for dialysis has been responsible for a number of patients requiring transfusion to treat resultant hemolytic anemia, and was a possible factor in an increased mortality (death) rate among the dialysis center patients during the 5 months after the chloramine exposure when compared to the 12 months before the chloramine exposure.

Treatment Alternatives

While chloramines are not a drinking water health concern to humans generally, their removal improves the taste and odor of drinking water. Chloramines are small, stable molecules with no net charge making them difficult to remove by distillation, reverse osmosis, and ion exchange resins. Due to the reaction of aqueous chlorine with organic nitrogen, chloramines also present a concern for municipal water systems utilizing chlorine as a method of disinfection. The most effective nonchemical method for removing chloramines is by activated carbon (C*). Activated carbon does not adsorb chloramines but rather removes them through its ability to act as a catalyst for the chemical breakdown of chloramines to innocuous chlorides in water. This catalytic reaction involves the formation of a carbon oxide intermediate (CO*). This reaction is as follows:

$$NH_2Cl + H_2O + C^* = NH_3 + Cl^- + H^+ + CO^*$$

$$2NH_2Cl + CO^* = N_2 + 2Cl^- + 2H^+ + H_2O + C^*$$

Fine mesh sizes of activated carbon remove chloramines more efficiently since they have greater surface areas and allow faster access to catalytic sites. Also, activated carbon that has been "acclimated" to achieve increased carbon oxide sites improves chloramine removal. For new activated carbon, initial dosing with chlorine to preoxidize the carbon may result in more effective chloramine removal. A bed contact time of 10 minutes or greater is required for complete catalysis of chloramines. New types of activated carbons (bituminous coal-based) have been developed with increased catalytic activity that are especially effective at the removal of chloramines. These new “catalytic” carbons are marketed with a peroxide number (rate of hydrogen peroxide decomposition) instead of the traditional iodine adsorption number. The chloramine removal capacity of activated carbon is dependent upon pH. Catalytic carbons have demonstrated increased chloramine removal efficiency at higher pHs.

Ammonia (NH_3), chloride (Cl^-), and nitrogen gas (N_2) are produced by the catalysis of monochloramine. The removal of these catalytic byproducts can be achieved by additional treatment with ion exchange resins or by reverse osmosis.

The treatment methods listed herein are generally recognized as techniques that can effectively reduce the listed contaminants sufficiently to meet or exceed the relevant MCL. However, this list does not reflect the fact that point-of-use/point-of-entry (POU/POE) devices and systems currently on the market may differ widely in their effectiveness in treating specific contaminants, and performance may vary from application to application. Therefore, selection of a particular device or system for health contaminant reduction should be made only after careful investigation of its’ performance capabilities based on results from competent equipment validation testing for the specific contaminant to be reduced.

As part of point-of-entry treatment system installation procedures, system performance characteristics should be verified by tests conducted under established test procedures and water analysis. Thereafter, the resulting water should be monitored periodically to verify continued performance. The application of the water treatment equipment must be controlled diligently to ensure that acceptable feed water conditions and equipment capacity are not exceeded.

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Association makes no recommendations for the selection of a treatment system, and expressly disclaims any responsibility for the results of the use of any treatment method or device to reduce or remove a particular contaminant.

ACKNOWLEDGEMENT

WQA wishes to express sincere appreciation for the unselfish contributions of the following members of WQA who contributed their time and expertise toward the completion of this bulletin.

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This reference document is published by:

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PRINTED IN USA 03/05