IBT Bulletin

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Free Chlorine, Bound Chlorine, Chloramine and Total Chlorine

Bleach/chlorine is the most cost effective disinfectant and is used extensively in dialysis clinics. Its use varies from light duty application in surface sanitation to heavy duty disinfection of medical devices or removal of microorganism infections in piping systems. Advantage of chlorine over peroxide type disinfectants is that chlorine not only is a strong oxidant, it also is capable of breaking tough chemical bounds found in cell walls or biofilms. Correct and effective use of bleach/ chlorine requires understanding of the chemical nature the disinfectant. The purpose of this brief article is to answer some basic questions related to its application, particularly in hemodialysis settings.

What is free chlorine?

When chlorine gas dissolves in water, it forms hypochlorous acid which in an alkaline solution turns into hypochlorite. Hypochlorite is the active form of chlorine and exists as a free ion in solution. It is, therefore, commonly referred to as free chlorine. Common bleach contains sodium hypochlorite, the same active ingredient as the free chlorine from chlorine gas.

What is chloramine or bound chlorine?

Chloramine is the product of the chemical reaction between chlorine and an amine compound. The term chloramine is a short name for chloro-amine. Amine compounds are organic chemicals with an amine group. Amine groups exist in several different forms. The simplest amine group is ammonia which has a chemical structure of NH_3.

Ammonia is often added to water during water treatment to convert and stabilize the chlorine in the form of chloramine. Chlorine in chloramine can revert back to free chlorine and exert its oxidative activity. The process, however, is slow and only a small fraction of chlorine is released at a given time. In effect, chloramine functions like a slow release medication in the water disinfection process. Since chloramine is less reactive than free chlorine, it will not form other chlorinated compound such as trichloromethane which would normally occur with high levels of free chlorine. Trichloromethane is a cancer causing agent.

Each of the hydrogens on the ammonia molecule can be replaced by chlorine. Depending on the concentration of chlorine, when one or two or all three of the hydrogens is replaced by chlorine, the resulting chloramine is called monochloramine, dichloramine or trichloramine, respectively. The three chloramines co-exist in equilibrium. In the municipal water, monochloramine is the predominant species.

When chlorine reacts and binds to other molecules such as in chloramine, it is also called bound chlorine. Not all the bound chlorine can reverse back to free chlorine, and for that which does the process is very slow and the reactivity minimal.

Is chloramine more toxic than chlorine?

There is a common misconception that chloramine is more toxic than free chlorine. This is mainly derived from the observation that chloramine will cause more hemolysis and form oxidized hemoglobin and Heinz bodies compared to free chlorine. The fact is that in the purified red cell suspension, free chlorine is as toxic as chloramine in causing hemolysis. The apparent difference in toxicity is due partially to the fact that the free chlorine reacts much faster and is unstable. It is rapidly consumed as soon as it comes into contact with blood, and before it is able to reach the red blood cells.

Although free chlorine is short-lived and more easily destroyed when it comes into contact with blood, it does not just disappear. Chlorine is eliminated at the expense of other valuable blood components, most notably the antioxidants. The antioxidants serve as oxidant/free radical scavengers and protect our body from the formation of cancer. Chronic exposure to chlorine will increase the potential of oxidative stress and reduce the body's ability to fight against cancer.

One other cause of the myth about free chlorine and chloramine is from the fact that the maximal allowable levels in water as recommended by the Association for the Advancement of Medical Instrument (AAMI) for free chlorine is 0.5 ppm, five times higher than 0.1 ppm limit for chloramine. One potential dangerous scenario from such different recommendations is that a clonic may allow the presence of free chlorine to be as high as 0.5 ppm as long as the chloramine is less than 0.1 ppm. and still be considered safe within the AAMI recommended standards.

How to remove chlorine from water?

Activated carbon probably is the most common and cost effective medium in removing chlorine. Chlorine is removed by reacting with carbon. When carbon is activated, the elementary carbon is capable of reacting with chlorine oxidants. The effectiveness of an activated carbon is determined by iodine number which is a measurement of how well the carbon reacts with iodine. Both iodine and chlorine have similar oxidative reactivity. The effectiveness of carbon in removing of chlorine is dependent on the reactivity of the chlorine species and the contact time. Free chlorine being the most active form of chlorine can be removed by carbon more readily and require shorter contact time than chloramines such as monochloramine from ammonia. Some chloramine may not be removed by carbon or may require much longer contact time. Fortunately, those chlorine species may subsequently be removed by reverse osmosis (RO) and discharged into the rejected water without reacting with the RO membrane.

Some chlorine in the form of bound chlorine may also be removed by adsorption with carbon. The total surface area of the carbon bed determine the total capacity of the carbon for reaction and adsorption.

There are other media available which supposedly have more reducing potential than activated carbon in reacting with chlorine. However, their use in the dialysis community does not seem to be common, perhaps because of the cost and lack of established safety for medical application. Another approach for removing chlorine is addition of a reducing substance such as ascorbic acid in the water. Such an approach appears to be simple and cost effective. However, it probably is used only as a supplement to carbon tank treatment.

How to measure chloramine?

There is no direct chemical method for measuring chloramine. Chloramine is indirectly estimated by calculating from the results of total and free chlorine. Since total chlorine is the sum of free chlorine and chloramine, the chloramine therefore is total chlorine less free chlorine.

When determined with a DPD reagent, free chlorine is at least 10 times more reactive than chloramine. Reaction with free chlorine is complete in less than 15 seconds. On the other hand, chloramine reacts very slowly without an activator. Activator is added to the total chlorine reagent to achieve complete reaction of both free chlorine and chloramine. It is, therefore, critical that the color of the free chlorine test be read in 15 seconds before any contribution of color from chloramine, and the color of total chlorine be read at 5 minutes. Inaccurate results occur when the strict timing requirements are not followed. Furthermore, contamination of activator from the total chlorine test into the free chlorine test causes falsely high free chlorine result and consequently falsely low chloramine result which can then be misjudged as within the safe level of the treated water.

Can I use total chlorine to monitor carbon tank function without determining the free and total chlorine in order to calculate the chloramine level?

This is one of the most commonly asked questions in water treatment. In fact, many clinics have already adapted such practice. The key is to monitor total chlorine at 0.1 ppm level.

Total chlorine is the measurement of all active chlorine species, including free and bound chlorine (chloramine). The amount of chloramine is calculated by subtracting free chlorine from the total chlorine. Since chloramine is part of the total chlorine, if the total chlorine is less than 0.1 ppm, the amount of chloramine will have to be less than 0.1 ppm. AAM1 standard for chloramine is 0.1 ppm or less. When monitoring the total chlorine at 0.1 ppm, it not only meets but exceeds the AAMI standard for the maximal allowable level for chloramine. Performing both free and total chlorine not only is time consuming, it is also prone to errors which may result in under estimation of chloramine level. The reality is that when the carbon is exhausted or if a channel is created, very likely both free chlorine and chloramine will appear in the post carbon water. Appearance of either free chlorine or chloramine in the post carbon water would equally indicate sub-optimal condition of the carbon tank. A reagent strip such as WaterCheck 2 from IBT which is sensitive to less than 0.1 ppm of total chlorine provides an easy and convenient way of monitoring the total chlorine in the post carbon water.

What is the effective concentration of chlorine/bleach?

Two major forms of chlorine disinfectant are hypochorite as in bleach and chlorine dioxide. Although chlorine dioxide is occasionally used in water treatment plants in combating algae problems, most dialysis clinics almost exclusively use chlorine/bleach for disinfection. The effectiveness of the bleach/chlorine disinfectant depends on the concentration of chlorine in the solution which further depends on the type of application. The Center for Disease Control recommends a concentration of 500 ppm for sanitation of working surfaces. However, for disinfection, a much higher concentration is required. In most applications, commonly used levels of chlorine are in the range of 1000 to 5000 ppm. The contact time also plays a key role in the effectiveness of the chlorine solution. Most applications use a contact time between 3 to 10 minutes. The choice of the combination of concentration and contact time depends on the specific application and one should consult with the manufacturer of the specific device.

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