Drinking Water Disinfection – A History and Improved Monitoring Techniques

by

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History

In many countries we take for granted the availability and reliability of safe drinking water. A recent trip outside of the US reminded me of this fact when I saw notices in the hotel rooms stating the drinking water met specific standards and was safe to drink however, my friends from the country emphatically warned me to not drink the water.

The relationship between clean drinking water and health has been known for centuries. Clear water was considered to be clean water and swamp water was associated with fever and disease.

Disinfection has been applied for centuries, two basic rules dating back to 2000 B.C. state that water must be exposed to sunlight and filtered with charcoal and that impure water must be purified by boiling the water and then dipping a piece of copper in the water seven times, before filtering the water. Records of ancient civilizations boiling water and storing water in silver jugs were found. Water purification was performed with copper, silver, and electrolysis.

Disinfection has been performed for several decades however, the mechanism has been known for only one hundred years. The microscope was developed in 1680 however it took scientists another two hundred years before they started using the microscope to distinguish microorganisms and other pathogens. In 1685 Italian physician Lu Antonio Porzo developed the first multiple filter. The filter consisted of a settling unit and a sand filtration unit. In 1746 the first patent for a filter design consisting of wool, sponges and charcoal, which was applied in households by 1750, was issued in France.

Humans have suffered from water-borne diseases such as cholera, typhoid, and the plague. In 1854 a cholera epidemic caused many deaths in the city of London. An English doctor, John Snow, discovered that the cholera epidemic was caused by a contaminated water pump. He prevented the spread of the epidemic by closing down the contaminated water pump. After that scientists have performed bacteriological studies to research the development, existence, and identification of microorganisms and the removal of microorganisms from drinking water.

In the nineteenth century the effect of disinfectants, such as chlorine, was discovered. Since 1900 disinfectants have been largely applied by drinking water companies to prevent water-borne diseases and to improve water quality and reduce the incidence rate of water-borne diseases as shown in figure 1.

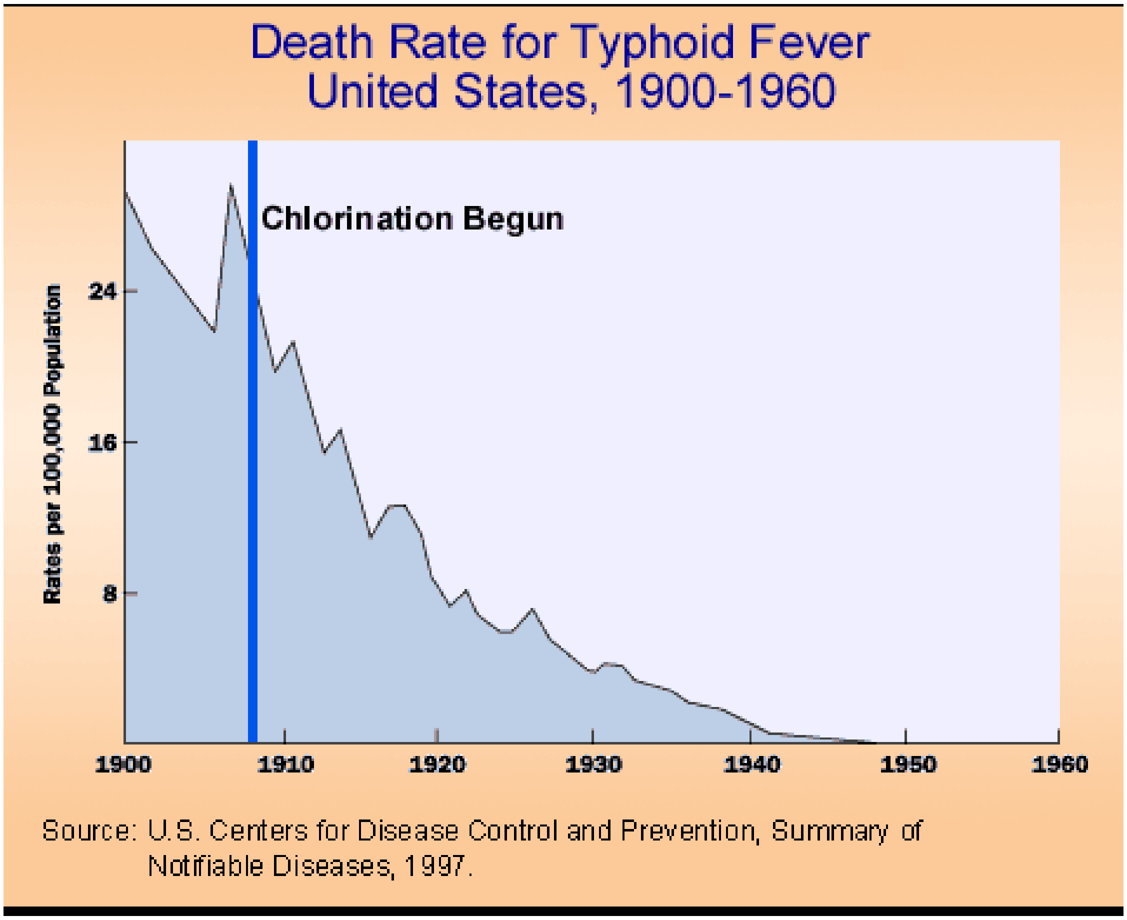


Figure 1: The effect of chlorination in reducing deaths by typhoid fever.

Disinfection of Drinking Water

Disinfection of drinking water can be accomplished in a number of ways using various disinfectants or combinations thereof. The following is a list of disinfectants employed however chlorine is the most common disinfectant employed.

1. Chlorine
    a. Gaseous
    b. Sodium hypochlorite (liquid bleach)
2. Chlorine dioxide
3. Ozone (Typically followed by chlorination to ensure residual in the distribution system)
4. Monochloramine
5. UV (Typically followed by chlorination to ensure residual in the distribution system)
6. Hydrogen Peroxide (Typically followed by chlorination to ensure residual in the distribution system)

Chemistry of Chlorine

How does chlorine actually carry out disinfection? Chlorine is a strong oxidizer. Depending on pH, the reaction of HOCl and water further yields equilibrium between hypochlorous acid and hypochlorite ion as shown in figure 2. Hypochlorous acid (HOCl) is approx. 70-90 times stronger oxidant then the hypochlorite ion “OCl^-” which is predominant at higher pH’s. Efficiency of disinfection with free chlorine decreases significantly with an increase in pH value.

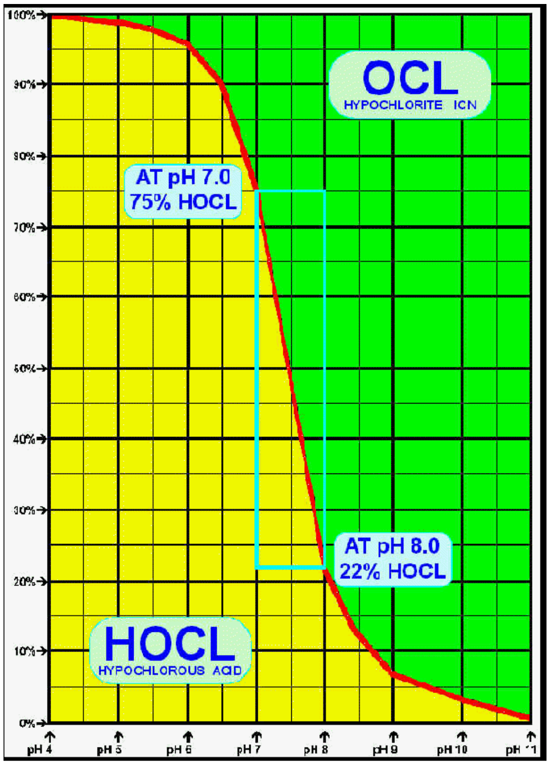


Figure 2: pH dependent equilibrium of chlorine

The further dissociation, along with the two types of "hypos" (mainly hypochlorous acid which is electrically neutral), can penetrate the cell walls of the organism and displace molecules needed to survive. The organism can no longer function or replicate and eventually dies as shown in figures 3 and 4.

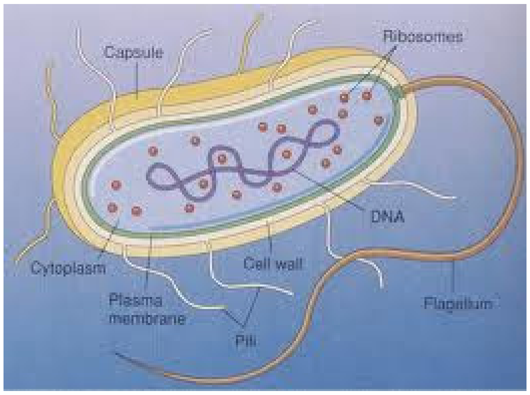


Figure 3: Example of bacteria.

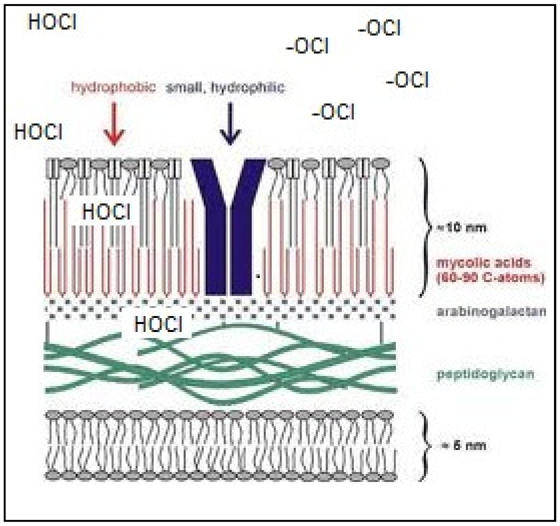


Figure 4: Illustration of how HOCl penetrates cell wall due to neutral charge.

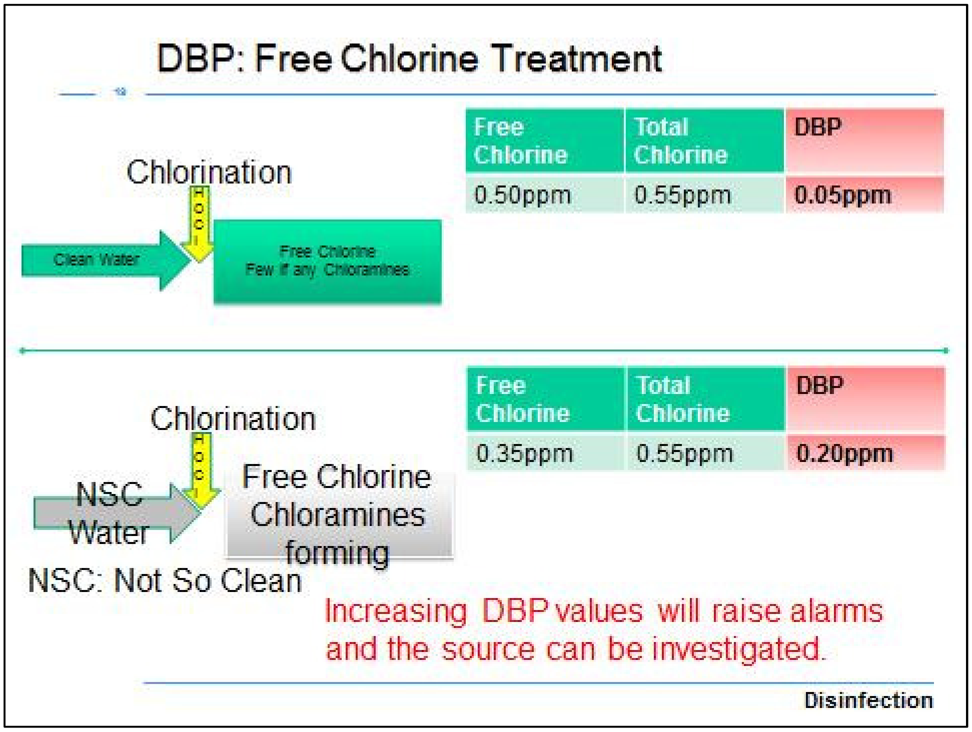
Free chlorine is a powerful oxidant and reacts rapidly with organic and inorganic matter. As a result, the strong disinfectant residual it initially provides may not persist as long as necessary within the distribution system. Free chlorine can readily react with organics to form unwanted disinfection byproducts (DPBs) such as trihalomethanes (THMs) and haloacetic acids (HAAs).

Safe Drinking Water Act of 1974

The Safe Drinking Water Act (SDWA), enacted in 1974, is the main federal law that ensures the quality of Americans' drinking water. Under SDWA, EPA sets standards for drinking water quality and oversees the states, localities, and water suppliers who implement those standards. The law was amended in 1986 & 1996 requiring many actions to protect drinking water and its sources: rivers, lakes, reservoirs, springs, and ground water wells.

Amendments to the SDWA in 1996 require EPA to develop rules to balance the risks between microbial pathogens and disinfection byproducts (DBPs). The Stage 1 Disinfectants and Disinfection Byproducts Rule and Interim Enhanced Surface Water Treatment Rule, promulgated in December 1998, were the first phase in a rulemaking strategy required by Congress as part of the 1996 Amendments to the Safe Drinking Water Act.

The Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 DBPR) builds upon the Stage 1 DBPR to address higher risk public water systems. This final rule strengthens public health protection by tightening compliance monitoring requirements for two groups of DBPs, trihalomethanes (TTHM) and haloacetic acids (HAA5). Stage 2 DBPR requires systems to perform a system evaluation to identify the locations with high DBP's which become the systems compliance sampling points. This has led many municipalities to employ chloramination to minimize formation of THM and HAA. Figure 5 illustrates a profile of water containing few impurities to react with chlorine to for disinfection by-products (DBP's) as well as water containing greater levels of impurities resulting in more DBP formation.



DBP: Free Chlorine Treatment

Free Chlorine	Total Chlorine	DBP
0.50ppm	0.55ppm	**0.05ppm**

Free Chlorine	Total Chlorine	DBP
0.35ppm	0.55ppm	**0.20ppm**

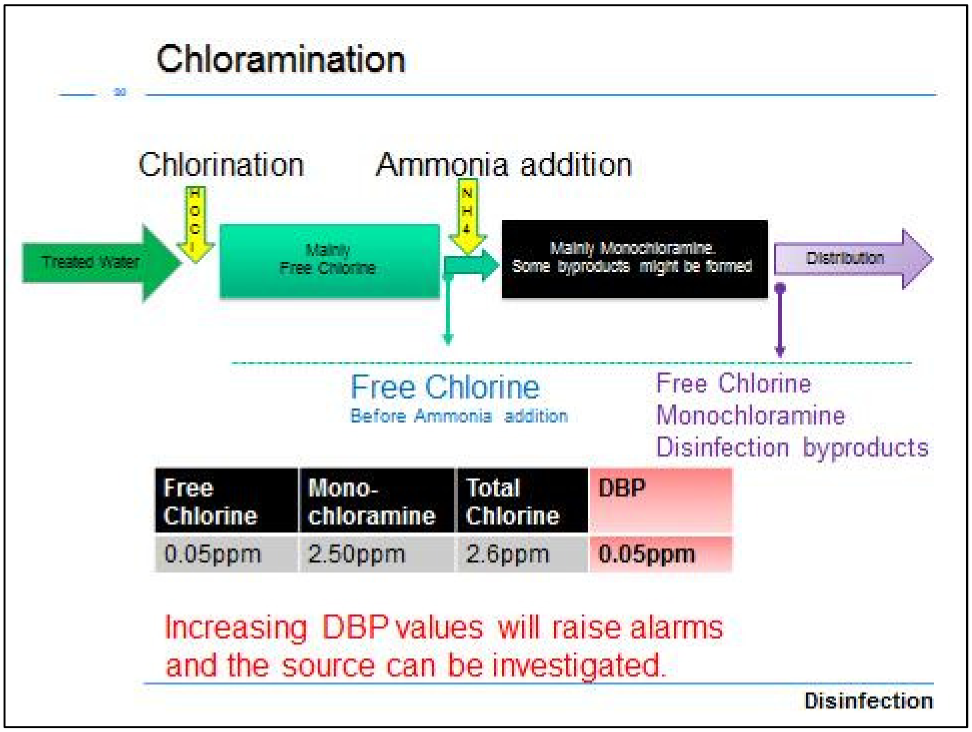
NSC: Not So Clean

Increasing DBP values will raise alarms and the source can be investigated.

Disinfection

Figure 5: Illustration of DBP's formed in clean and "not so clean" water.

Chloramination results in lower concentrations of THM and HAA. Proper control of the chloramination process yields lower concentrations of DBP's thereby providing high quality drinking water for the public. Figure 6 illustrates the chloramination process and control of the process by monitoring the free, monochloramine, and total chlorine.



Chloramination

Free Chlorine	Mono-chloramine	Total Chlorine	DBP
0.05ppm	2.50ppm	2.6ppm	**0.05ppm**

Increasing DBP values will raise alarms and the source can be investigated.

Disinfection

Figure 6: Chloramination process and monitoring of the process.

Disinfectant Residual Monitoring

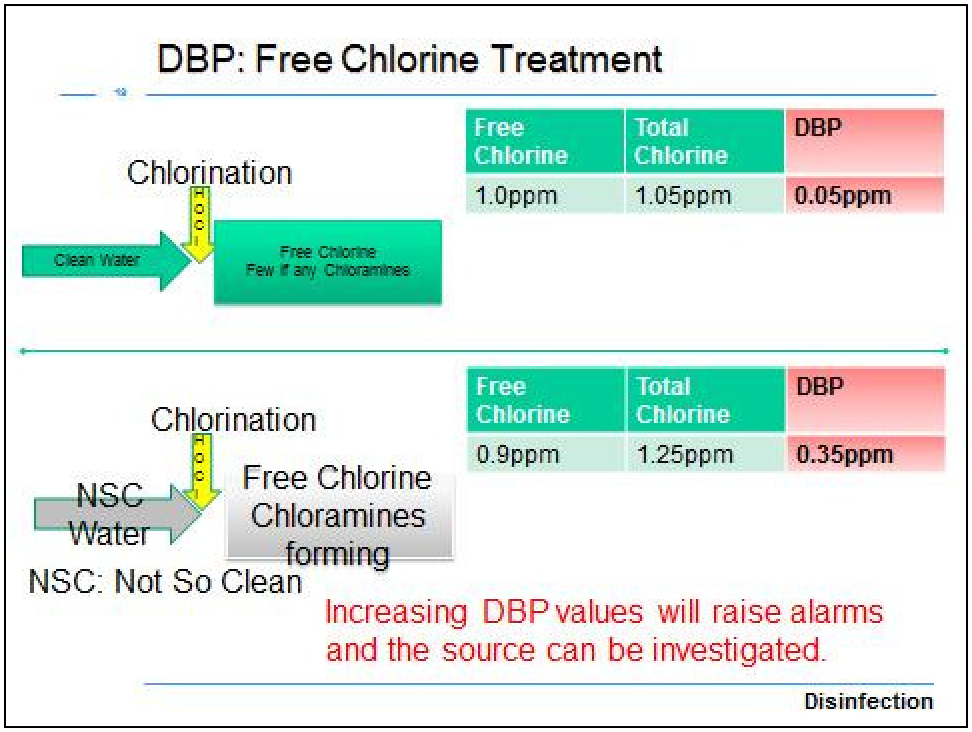
Federal and state regulatory agencies regulate the monitoring of disinfectant residuals as well as the concentration of the disinfectant employed. Therefore if a system is using chlorine as their disinfectant they must maintain the required concentration of free chlorine and monitor the chlorine residual in accordance with EPA Method 334.0. Therefore the organization must monitor the free chlorine. Most systems use continuous monitoring either Amperometric or DPD based measurement systems. However monitoring the free, monochloramine, total chlorine, and combined chlorine provides the operator with much more information regarding the water quality. As seen in figure 5, “clean” water contains few impurities thereby DBP production is minimized. If greater levels of impurities are present higher concentrations of DBP’s are produced. This can be readily observed if comprehensive chlorine monitoring is performed. This can be accomplished as follows:

- Free Residual Chlorine
  - Red color formation with DPD and buffer
  - Reaction time of 3 – 5 sec
  - According ISO 7393-2 / EPA 334.0

- Total Chlorine 1 – TC1 (Sum of free chlorine and monochloramine)
  - Additional Potassium Iodide (KI) is added to the buffer.
  - Red color formation with DPD
  - Reaction time of 3-5 sec
  - Monochloramine calculated by subtracting free chlorine determined in previous step from Total Chlorine 1

- Total Chlorine 2 – TC2 (Sum of all chlorine species)
  - Red color formation with DPD, buffer and KI
  - Reaction time of 120 seconds!
  - Combined (di- and tri-chloramines determined by subtracting TC1 from TC2

This allows the operator to be aware of when the water supply is experiencing contamination such as by farming whereby fertilizer run-off can increase the ammonia concentration in surface waters or ground waters under the influence. An example is shown in figure 7.



DBP: Free Chlorine Treatment

Chlorination

HOCl

Clean Water

Free Chlorine
Few if any Chloramines

Free Chlorine	Total Chlorine	DBP
1.0ppm	1.05ppm	0.05ppm

Chlorination

HOCl

NSC Water

Free Chlorine
Chloramines
forming

NSC: Not So Clean

Free Chlorine	Total Chlorine	DBP
0.9ppm	1.25ppm	0.35ppm

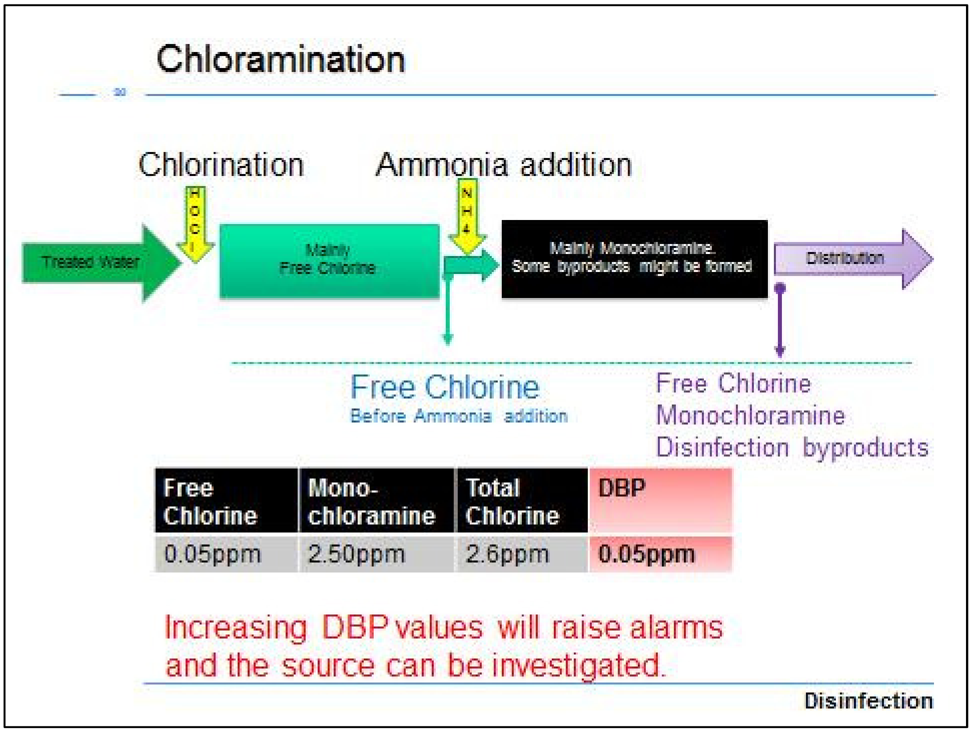
Increasing DBP values will raise alarms and the source can be investigated.

Disinfection

Figure 7: Example of seasonal influence on water quality.

Chloramination

For systems employing chloramination and analyzer that can monitor free, monochloramine, total chlorine, and combined chlorine provides sufficient data and control capability to properly control the chloramination process. Most systems maintain ≤ 0.05 ppm of free chlorine to ensure free ammonia is not present to reduce the risk of nitrification. Also, the free residual must be maintained at a low level to avoid formation of di and tri-chloramines. Figure 8 illustrates a desirable profile for chloramination. The monochloramine concentration is slightly less than the total chlorine concentration indicating there is very little dichloramine formed. The presence of 0.05 ppm free chlorine ensures there is no free ammonia present which reduces the risk of nitrification. Ana analyzer that can provide this level of monitoring is ideal for monitoring and controlling chloramination. Figure 9 is data from a water system employing chloramination. As illustrated the monochloramine concentration is slightly less than the total chlorine concentration. The free chlorine is consistently very low (≤ 0.05 ppm) much of the time, however at one point the free chlorine concentration increased resulting in increased dichloramine formation and reduce monochloramine concentration. The operator took corrective action to bring the process under control. The ammonia feed system also failed resulting in reduced monochloramine and total chlorine concentration until ammonia feed was resumed.



Chloramination

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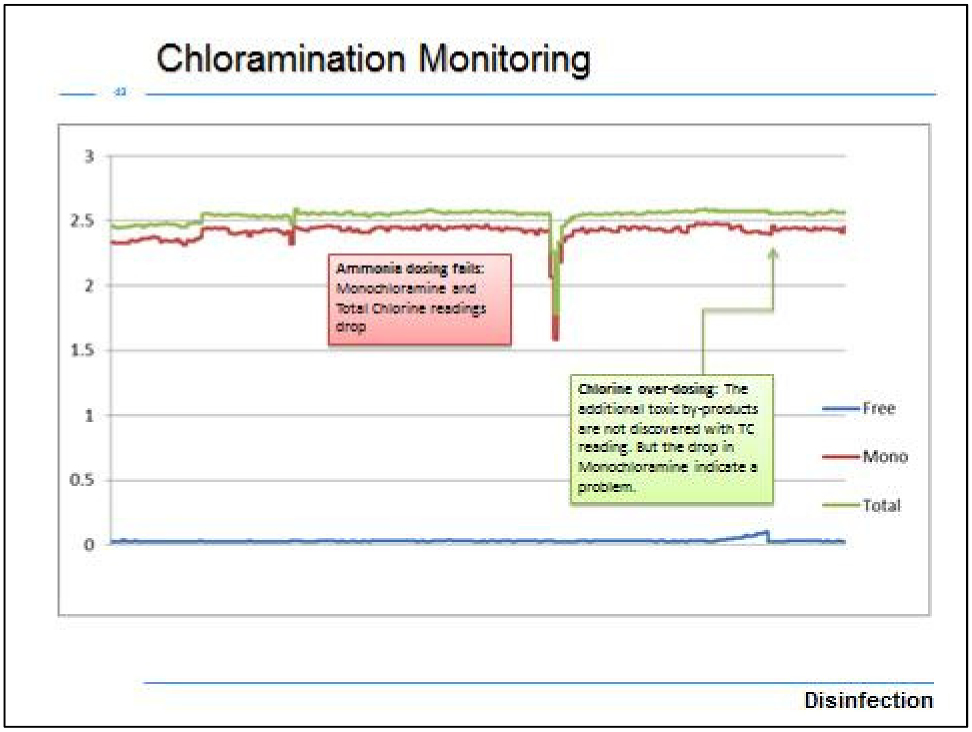
Disinfection

Figure 8: Chloramination monitoring profile.



Chloramination Monitoring

Ammonia dosing fails: Monochloramine and Total Chlorine readings drop

Chlorine over-dosing: The additional toxic by-products are not discovered with TC reading. But the drop in Monochloramine indicate a problem.

Disinfection

Figure 9: Municipality chloramination process monitoring data.

Summary

Clean, safe drinking water is essential for public health. Man has been aware of this and practiced various forms of disinfection for centuries. In the 1900's disinfection of drinking water with chlorine became the standard practice which has greatly reduced water-borne disease incident rates where properly practiced. As concerns about the health effects of disinfection by-products grow the regulatory agencies place more stringent limits on those species of concern thereby impacting treatment and disinfection processes. Monitoring not only the free chlorine but the monochloramine, total chlorine, and combined chlorine provides the operator with much more data regarding water quality and allows the operator to refine his treatment and disinfection processes to improve water quality. It alerts him/her of changes is raw water quality which impacts finished product quality allowing them to take action and if necessary install new processes for treatment and/or disinfection to provide the best quality drinking water.

Figure 10: Swan AMI Codes II CC

- The Swan AMI Codes II CC reliably monitors:
  - Free chlorine
  - Monochloramine
  - Combined chlorine (di- and tri-chloramine)
  - Total chlorine.
- The operator is informed about measurement ***validity*.**
- The integrity of the analyzer can be verified within minutes.
- Reagent level is continuously monitored.
- Process pH monitoring is optional.

To see more information on the Swan AMI Codes II CC click on the link below:

Swan AMI Codes II CC Datasheet

References: