

## ANALYSIS OF DISINFECTIONS

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### **Summary**

It is important that tap water is not contaminated by pathogenic organisms, and that it is hygienically safe. Since it is not possible to completely remove microbes in water by sedimentation and filtration, tap water must be fully disinfected to secure hygienic safety in distribution systems. There are various kinds of disinfectants such as chlorine and chlorine agents, chlorine dioxide, iodine, ozone or UV radiation process. Among these, chlorine is the most widely used in the disinfection process because its disinfection effect is most complete.

The injection method is selected by considering the type of chlorine agent, the volume of treated water and working conditions. Safety equipment and neutralizing systems should have sufficient capacity to prevent serious accidents of chlorine gas leakage.

In order to assess the efficiency of disinfection, Ct value that is derived by the concentration of dose of disinfectant and time for disinfection process is a commonly used surrogate parameter. Among the disinfectants including chlorine, not only does the efficiency differ, from the point of inactivation, but also the development of mutagenicity by disinfection by-products also differ.

## **1. Introduction**

It is important that tap water is not contaminated by pathogenic organisms, and that it is hygienically safe. Since it is not possible to completely remove microbes in water by sedimentation and filtration, tap water must be fully disinfected to secure hygienic safety in distribution systems. For this reason, purification facilities, both small and large, and irrespective of treatment methods, are recommended to provide disinfection systems.

There are various kinds of disinfectants such as chlorine and chlorine agents, chlorine dioxide, iodine, ozone or UV radiation process. Among them, chlorine is the most widely used in the disinfection process because disinfection effect is most complete—it can easily disinfect water of large volume, and the effect is long-lasting. The disadvantages, however, are that organic chlorine compounds such as trihalomethanes are generated, a strong odor appears by reaction with certain substances, and the disinfection effect is weakened by reaction with ammonium nitrogen.

Chlorine agents include liquefied chlorine, sodium hypochlorite and calcium hypochlorite (including the high-grade bleaching powder). Chlorine agents will be selected by considering the facility scale and the conveniences of handling, and the feed rate, which differs between water qualities. This is determined through elaborate study of water quality. The facility capacity will be determined based on these results.

It is necessary that storage facilities for chlorine agents have appropriate capacity to match the quantity of use and the injection systems, including standby injection systems. These should be well capable of measuring and feeding between the maximum and minimum feeding rates. The injection method will be selected by considering the type of chlorine agent, the volume of treated water and working conditions, including constant feeding or flow proportional feeding. Neutralizing systems should have a sufficient neutralizing capacity to prevent serious accidents in case of chlorine gas leakage.

## **2. Chlorine in water**

As already stated, chlorine agents include liquefied chlorine, sodium hypochlorite and calcium hypochlorite (including the high-grade bleaching powder). Additionally, however, sodium hypochlorite is produced by electrolysis at purification plants.

Liquefied chlorine is chlorine gas which is liquefied and charged in a container. Since chlorine gas is heavier than air, has a pungent odor and strong toxicity, great care should be taken in handling it in compliance with the stringent legal requirements. Sodium hypochlorite is a pale yellow liquid with an effective chlorine concentration of 5 to 12%

and is a strong alkali. The higher the concentration, the less the stability, and the effectiveness of chlorine reduces during storage. Both the safety and handling ease of sodium hypochlorite are better than those of liquefied chlorine.

Since oxygen bubbles released from chlorinated water accumulate in the pipes and the pumps, and interferes with water flow, elaborate consideration is required. The sodium hypochlorite produced by a house generation system is a weak solution with 1% or less of effective chlorine concentration. Accordingly, it is relatively free from bubble accumulation compared with commercial sodium hypochlorite, but use of this system makes the facility more complicated. Calcium hypochlorite is available in powder, granule or tablet form, and, as the effective chlorine concentration reaches 60% or more, the storage efficiency is high.

When selecting a chlorinating agent, besides the above-mentioned characteristics of the chlorine agents, the convenience of the maintenance and also safety measures of the facility against disasters must be taken into account. Generally, in smaller and medium-scale waterworks, it is desirable to use a commercial or house generated calcium hypochlorite. For relatively large-scale waterworks, however, commercial sodium hypochlorite is sometimes used. Additionally, for emergency stocks, such as disasters, sodium hypochlorite is recommended due to its easy handling and chemical stability.

When chlorine is dissolved in water, it generates hypochlorous acid (HClO) and hydrochloric acid. Hypochlorous acid is partly dissociated into hypochlorous acid ion (ClO<sup>-</sup>) and hydrogen ion. This reaction is reversible and the process is in equilibrium at the pH value and water temperature.

In the case of chlorine:



In the case of sodium hypochlorite:



Both hypochlorous acid (HClO) and hypochlorous acid ion (ClO<sup>-</sup>) are effective chlorine, but their sterilizing powers largely differ. Hypochlorous acid has stronger sterilizing power. Since the existence ratios of hypochlorous acid and hypochlorous acid ion vary as a function of pH, where hydrochlorous acid is increased at lower pH value, the disinfection power is higher at lower pH value.

Based on the equivalent chlorine quantity, sodium hypochlorite has twice the oxidizing power of hypochlorous acid ion. Therefore, the effective chlorine of sodium hypochlorite is twice of that of hypochlorous acid ion.



Hypochlorous acid and hypochlorous acid ion are called free chlorine or free residual chlorine. On the other hand, when water contains ammonium compounds, chlorine reacts with them and generates chloramines. Chloramines turn into monochloramine ( $\text{NH}_2\text{Cl}$ ), dichloramine ( $\text{NHCl}_2$ ) or trichloramine ( $\text{NCl}_3$ ) according to the pH value of the water. Monochloramine and dichloramine are called combined chlorine or combined residual chlorine.

The free chlorine and combined chlorine have different sterilizing power. To obtain the same result under optimal condition with the same contact time, 25 times as much combined chlorine is required as free chlorine, or using the same quantity, approximately 100 times the contact time.

The dosage of chlorine for disinfection should be determined based on the chlorine demand of the disinfection using the free chlorine, and the chlorine consumption of the disinfection using the combined chlorine. Generally, the chlorine demand equals the chlorine consumption for water of good quality, but they greatly differ in water containing high ammonium nitrogen.

Figure 1 shows the relationship between chlorine dosage and residual chlorine quantity, and it is classified into types I, II and III, depending on the water quality. Type I is the case of water which does not contain organic matter nor any reducing matter. This type actually does not exist. Type II is the case of water which has a certain chlorine demand, where the free residual chlorine is detected proportionally as the chlorine dosage increases. Type III is the case of water containing ammonium compounds and organic nitrogen compounds (albuminoidal, amino acid attune, etc.), where the combined residual chlorine is generated by feeding chlorine, and the quantity increases as the quantity of the fed chlorine increases. However, after reaching a certain quantity, the residual chlorine decreases, nearly to zero, despite the increase in chlorine dosage (because chloramines are decomposed by excess chlorine). When the chlorine dosage is increased further, then the free residual chlorine is increased proportionally to the increase.

In the case of type II, the chlorine feed to point a. is the chlorine demand and the chlorine consumption. For type III, the chlorine feed to point b is the chlorine demand, and the chlorine dosage up to point c is the chlorine consumption.

This refers to a method by which disinfection is conducted using the free residual chlorine to cope with water quality containing ammonium nitrogen, which generates chloramines. The point c of type III is called the breakpoint, and a method applying chlorine so as to detect the free residual chlorine exceeding the point is called breakpoint chlorination. Since the free chlorine has a strong sterilizing power, a thorough disinfection effect can be obtained.

When bacteria count is low and ammonium nitrogen exists at high level, as with groundwater, combined chlorine (chloramines) may be used for disinfection. For water in which ammonium nitrogen is derived from pollutants, imperfect disinfection may result with combined chlorine, so breakpoint chlorination is applied. However, when it is necessary to maintain residual chlorine for a long time, and when disinfection with combined chlorine is required to prevent an increase in color and offensive odor, first

chlorine is fed to decompose ammonium nitrogen and the generated chloramines, and then ammonium is added. For this purpose, liquefied ammonium may be used because it can be fed via the same chlorine injectors.

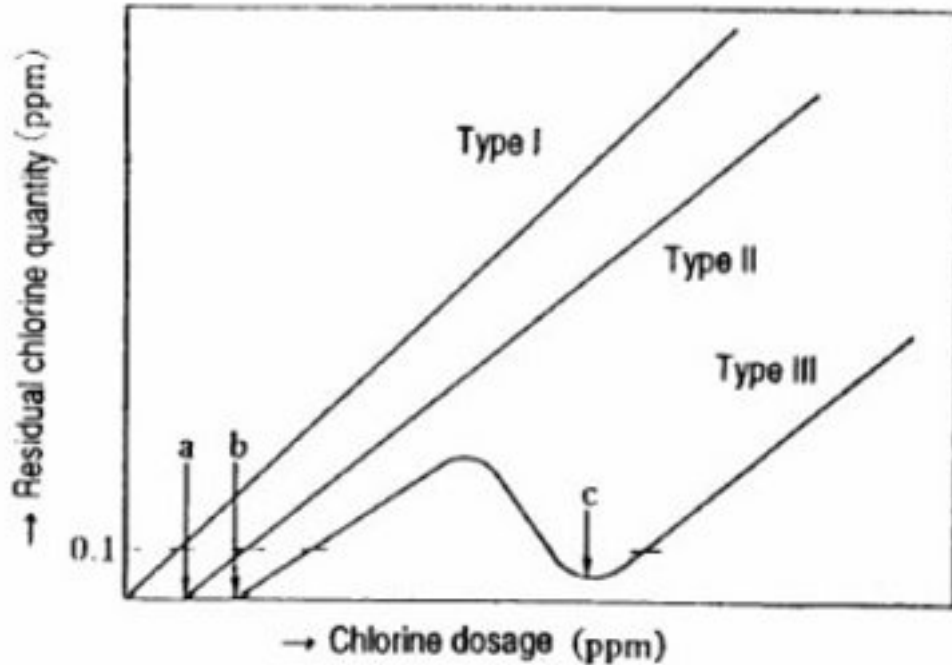


Figure 1. Relationship of chlorine dosage and residual chlorine quantity

When conducting disinfection with combined chlorine, an appropriate method should be used to allow thorough contact. If water is mixed from different water sources in a distribution line, different disinfection methods (one using free chlorine and the other using combined chlorine) should be avoided because it may waste residual chlorine.

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#### Bibliography

Braghetta, A., Jacangelo, J., Trussell, R. R., and Meheus, J. (1997). *The practice of chlorination: application, efficacy, problems and alternatives*. IWSA. [The report on chlorination prepared by the scientific and technology committee of IWSA.]

JWWA and JICA (1990). *Design criteria for waterworks facilities*. Japan Water Works Association and Japan International Cooperation Agency. [This book describes matters to be considered in promoting the new arrangement and improvement of waterworks facilities, the procedure for establishing a master plan, the contents of a master plan, and criteria and items of note for designing.]

Ministry of health and welfare, Japan (1999). The outline of review on water quality standards for drinking water.

Rook, J.J.(1977) Chlorination reactions of fluvic acids of natural waters, *J. Environ. Sci. Technol*, 11:478-482 [A traditional paper that first drew attention to generation of chlorination by-products.]

U.S. EPA (1998) Federal Register 40 CFR Parts, 141, and 142, Part IV (1998.12.16). [This contains a new U. S. concept for disinfectant and DBPs. A new standard for bromate is presented.]

WHO (2000) Disinfection and Disinfectant By-products, Environmental Health Criteria 216, International Programme on Chemical Safety, Geneva. [Disinfectant and DBPs are reviewed from various aspects. WHO guidelines are reviewed, with results.]

### Biographical Sketches

**Masanori Ando** is Director of Environmental Chemistry at the National Institute of Health Sciences, where he has been in office since 1991. He was admitted to Meiji Pharmaceutical University in 1963 and received the degree of Bachelor of Pharmacology in 1967. He commenced his professional carrier at National Institute of Hygienic Sciences in 1968. He served as a researcher in the Environmental Hygiene Chemistry Department. He was promoted to Senior Research Officer of the Department in 1983, then Section Chief in 1987. He obtained a Ph.D. in Pharmacology from the University of Tokyo in 1977. In 1995, the Institute changed its name to National Institute of Health Sciences. His research area covers environmental chemistry, analytical science, chemical toxicology, health science, exposure assessment, etc.

Dr. Ando has written Analytical Methods for Drinking Water. He has been the author or co-author of approximately 80 research articles.

**Yasumoto Magara** is Professor of Engineering at Hokkaido University, where he has been on faculty since 1997. He was admitted to Hokkaido University in 1960 and received the degree of Bachelor of Engineering in Sanitary Engineering in 1964 and Master of Engineering in 1966. After working for the same university for 4 years, he moved to National Institute of Public Health in 1970. He served as the Director of the Institute since 1984 for Department of Sanitary Engineering, then Department of Water Supply Engineering. In the meantime, he also obtained a Ph.D. in Engineering from Hokkaido University in 1979 and was conferred Honorary Doctoral Degree in Engineering from Chiangmai University in 1994. Since 1964, his research subjects have been in environmental engineering and have included advanced water purification for drinking water, control of hazardous chemicals in drinking water, planning and treatment of domestic waste including human excreta, management of ambient water quality, and mechanisms of biological wastewater treatment system performance. He has also been a member of governmental deliberation councils of several ministries and agencies including Ministry of Health and Welfare, Ministry of Education, Environmental Agency, and National Land Agency. He meanwhile performs international activities with JICA (Japan International Cooperation Agency) and World Health Organization. As for academic fields, he plays pivotal role in many associations and societies, and has been Chairman of Japan Society on Water Environment.

Professor Magara has written and edited books on analysis and assessment of drinking water. He has been the author or co-author of more than 100 research articles.