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# Water Chlorination/ Chloramination Practices and Principles

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**AWWA MANUAL M20**

*Second Edition*



**American Water Works  
Association**

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***Science and Technology***

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# Chapter 1

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## History of Chlorination and Chloramination

Chlorine was “discovered” in 1744 in an obscure laboratory in Sweden (AWWA 1973). Sixty-six years later in 1810, chlorine was identified as a chemical element and was named from the Greek word *chloros* (pale green), because of its characteristic color. However, it was not until several decades later that its use as a disinfectant was recognized.

Until the germ theory of disease was established around the mid-1880s, odors were thought to be responsible for transmitting diseases. As such, it was widely believed that the control of odors would limit the spread of infections. There is no question that the earliest applications of chlorine were aimed at controlling foul odors (Baylis 1935), even though, because of the unsophisticated techniques used, the chlorinous odor imparted to the treated water was sometimes just as, or more, objectionable than the odor it was meant to remove. It was not until well into the 1890s that chlorine and chlorine-containing products were evaluated and demonstrated to be effective disinfectants.

### ORIGIN OF WATER DISINFECTION

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Undoubtedly the disinfection of water has been practiced for millenniums, although probably with little or no understanding of the principles involved. Historical records indicate that the boiling of water had been recommended at least as early as 500 B.C. The earliest recorded use of chlorine directly for water disinfection was on an experimental basis, in connection with filtration studies in Louisville, Ky., in 1896. It was employed for a short period in 1897 in England, again on an experimental basis, to sterilize water distribution mains following a typhoid epidemic.

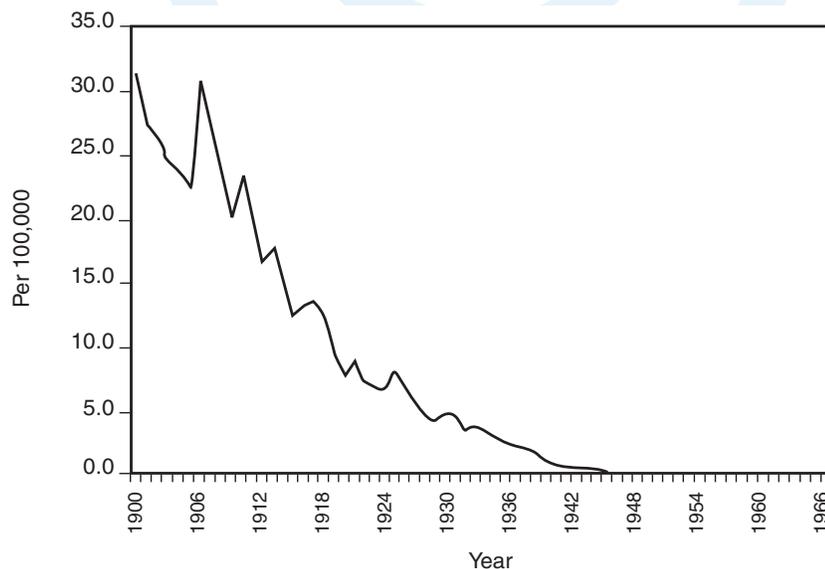
The first *continuous* use of chlorine for water disinfection was in 1902 in Belgium for the dual objective of aiding coagulation and making water biologically “safe.” In North America, the first continuous, municipal application of chlorine to water was in 1908 to disinfect the 40-mgd (151-ML/d) Boonton Reservoir supply of the Jersey City, N.J., water utility. Contested in the courts, the practice was declared to represent a public health safeguard, and this action paved the way for its rapid extension to other public water supplies throughout North America and elsewhere.

## RATIONALE OF WATER DISINFECTION

Waterborne diseases, such as typhoid, dysentery, and cholera, occurred with regularity in US water systems in the 1800s. The incidence rates were high in the early 1900s (e.g., more than 25,000 typhoid deaths in 1900) but decreased rapidly with the onset of chlorination (e.g., less than 20 deaths in 1960) (Laubusch 1964), as shown in Figure 1-1. The data provide similar results for other organisms.

With such a dramatic drop in illnesses and fatalities following the onset of chlorination, the need for feeding these chemicals was well justified. To date, chlorine has emerged as the disinfectant of choice primarily because of its effectiveness (Race 1918), efficiency, economy of operation, convenience, and the persistence of a chlorine residual. The unique properties of chlorine also make its use an acceptable technique for taste-and-odor control, algae and slime control, water-main disinfection, and many other purposes. However, chlorine has come under intense scrutiny because some of the by-products of the disinfection process may be carcinogenic. In spite of this, chlorine is expected to remain in wide use.

Water disinfection, as now ordinarily considered, involves specialized treatment for the destruction of harmful, and otherwise objectionable, “nuisance” organisms. Classically, disinfection processes have been employed to destroy or inactivate disease-producing (pathogenic) organisms—more particularly bacteria of intestinal origin. Such organisms can survive for weeks in the environment at temperatures near 70°F (21°C), or possibly even for months at lower temperatures. In addition to temperature influences, their survival in water depends on environmental, physiological, and morphological factors, such as pH, oxygen and nutrient supply, dilution, competition with other organisms, resistance to toxic influences, and ability to form spores. Whether these organisms actually will cause disease in humans upon ingestion depends on their virulence and concentration and also on the individual’s vulnerability or susceptibility to them.



\*Based on Vital Statistics of the United States 1937, 1938, 1943, 1944, 1949, 1960, 1967, 1976, 1987, 1992, Historical Statistics of the United States—Colonial Times to 1970 Part 1.

Source: *HealthSentinel.com*.

Figure 1-1 US typhoid mortality and disease rates

Water disinfection also encompasses the destruction of disease-producing organisms other than intestinal bacteria, but it does not necessarily imply the complete destruction of *all* living organisms (i.e., *sterilization*). Water disinfection processes seldom have been carried to the point of sterilization, which has been largely confined to the medical field. Among the other disease-producing organisms important in regard to water disinfection are a variety of viruses, intestinal protozoa, and some macro-organisms. In addition, many nuisance organisms of aesthetic or economic significance, both plant and animal, are sometimes vulnerable to disinfection and can be partially or completely controlled by suitable treatment.

## EVOLUTION OF CHLORINATION MATERIALS

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During the infancy of water chlorination, the only commercial sources of chlorine were dry chlorine-containing *compounds*, such as chlorinated lime (also called chloride of lime and bleaching powder) and sodium hypochlorite bleach solutions. The poor stability and variable effective chlorine content of the compounds then available caused many operating difficulties, and often inadequate disinfection dosages were used. Moreover, the comparatively crude equipment feeders yielded erratic results.

In 1909, liquid chlorine (the element in compressed form) became available commercially, and in the following year it was employed experimentally for water disinfection in Fort Myer, Va. The chlorine was added to the water by using a simple dry-gas feeder. In 1912, the first full-scale successful use of liquid chlorine was undertaken to control a recurring outbreak of typhoid in Niagara Falls, N.Y. In this case, a solution feeder was used. Two years later, improved equipment developed by C.F. Wallace and M.F. Tiernan to measure chlorine gas, dissolve it in water, and apply the solution was installed in Boonton, N.J., replacing the use of sodium hypochlorite bleach. These developments paved the way for the future extension of water disinfection techniques utilizing liquid chlorine.

Hypochlorite water chlorination gradually decreased in popularity, but it received renewed interest in 1928 with the commercial availability of high-test calcium hypochlorite, which was a more stable and active material than the various bleaching powders and solutions previously available. Today, there are three principal sources of chlorine for water disinfection and other chlorination treatment: (1) in elemental form, as a liquefied compressed gas (in commerce); (2) as "high-test calcium hypochlorite"; and (3) as chlorine bleach solutions (not to be confused with elemental liquid chlorine or with water solutions of chlorine gas).

## EVOLUTION OF CHLORINATION CONTROL PRACTICES

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Improvements in chlorine disinfection materials and in chemical feeders substantially contributed to the popularity and widespread adoption of water chlorination. Originally disinfection dosages were based largely on the application of fixed amounts of chlorine. Soon it became apparent that provisions were not being made for the effects of variations in water quality and the fluctuation in chlorine demand.

Gradually, the concept of varying chlorine dosage on the basis of residual chlorine was established, and iodometric methods for qualitative and quantitative assay of residual chlorine were developed. The use of orthotolidine as a qualitative indicator of residual chlorine was proposed in 1909, and later its use was extended quantitatively by the development of colorimetric standards. Between 1917 and 1919, chlorine disinfection was established on a scientific basis when the suitability and reliability of the orthotolidine test for even the smallest water supplies were demonstrated. Since then, a better understanding of water chlorination processes has brought many refinements in that test and in the development of other tests, such as the orthotolidine-arsenite colorimetric test to distinguish forms of residual chlorine, amperometric differential

titration, and various other differential chemical tests for available chlorine. In recent years, the use of orthotolidine reagent has been discontinued in favor of the safer and more stable *N,N*-diethyl-*p*-phenylenediamine (DPD) method. DPD is commonly used both for color comparison and titrimetric chlorine testing.

## DISCOVERY OF TRIHALOMETHANES

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As chlorination processes gained further acceptance, new discoveries were limited to refinements in the existing methods and chemistry (Connell 1996). It wasn't until the 1970s that trace organic chlorination by-products were discovered. In Holland, Rook identified that the reaction of chlorine with organic materials dissolved in water produced a class of compounds called trihalomethanes (THMs) (Connell 1996). The organics, usually humic and fulvic acids that originate in decaying vegetative growths, can be found in agricultural runoffs, aquifers, and natural vegetation.

The THMs were identified as possible cancer-causing agents, and their discovery in drinking water raised concerns about chlorination. Research began on the nature of the reactions that produce THMs, the concentrations of THMs considered unacceptable in drinking water, and methods to reduce or prevent their formation. The great rush of scientific work produced sufficient data to lead regulatory bodies in Europe and North America to set acceptable THM concentration levels in finished water and to determine ways to minimize THM formation in existing plants.

## HISTORICAL DEVELOPMENT OF CHLORAMINE

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It is likely that chloramines formed accidentally in wastewater and in waters containing natural ammonia for some time before this reaction was characterized. In the early 1900s, the chlorine-ammonia combination received attention when it was found that the cost of chlorination might be reduced if ammonia was added (Race 1918). The practice of chloramine treatment was adopted in 1916 at the treatment plant in Ottawa, Ont. The first installation in the United States was in 1917 in Denver, Colo. Both locations used ammonia and hypochlorite and noted improvements in taste and reductions in after-growth in the distribution system.

Additional utilities adopted the use of chlorine-ammonia in the years that followed, as listed in Table 1-1, and more than 400 utilities were using the process by 1938. Breakpoint chlorination was discovered in 1939, and thereafter, the use of chloramines declined. Chloramine usage was further reduced during World War II when ammonia was in short supply.

Chloramines were then used sparingly until the 1970s when trace organic chlorination by-products were discovered (THMs). As discussed earlier in this chapter, THMs are produced from the reaction of chlorine with natural organic materials (humic and fulvic acids) and were also identified as possible carcinogens.

Subsequent to the discovery of THMs in drinking water, chloramination received renewed attention because it produces less THMs than *free* chlorine under most conditions. Haloacetic acids (HAAs) were identified as chlorination disinfection by-products and a group of five of these compounds were regulated in 1998. This further supported the use of alternate disinfectant such as chloramines.

A common disinfection strategy is to provide primary disinfection with chlorine or another strong disinfectant and then use chloramine as the residual disinfectant. This combination reduces chlorine by-product formation that would occur in the distribution system but still satisfies the need to ensure microbiologically safe drinking water. The widespread use of chloramines may be affected in the future, however, as new information is available on the by-products of chloramination.

Table 1-1 Utilities with long experience of chloramines use

City	Approximate Start of Chloramination
Denver, Colo.	1917
Portland, Ore.	1924
St. Louis, Mo.	1934
Boston, Mass.	1944
Indianapolis, Ind.	1954
Minneapolis, Minn.	1954
Dallas, Texas	1959
Kansas City, Mo.	1964
Milwaukee, Wis.	1964
Jefferson Parish, La.	1964
Philadelphia, Pa.	1969
Houston, Texas	1982
Miami, Fla.	1982
Orleans Parish, La.	1982
San Diego, Calif.	1982

Source: Trussell and Kreft 1984.

## EVOLUTION OF CHLORAMINATION MATERIALS

The first observations of chloramine formation were in waters that contained ammonia. In addition, wastewater disinfection with chlorine often resulted in the formation of chloramines. Ammonia was initially added to water as aqua ammonia (liquid ammonium hydroxide) or ammonium salt solutions. Precipitation of calcium from water near the point of application prevented the widespread use of compressed ammonia gas. This issue was resolved and the use of anhydrous ammonia (gas) is now commonplace. The four forms of ammonia currently in common use are anhydrous ammonia ( $\text{NH}_3$ ), aqua ammonia ( $\text{NH}_4\text{OH}$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), and ammonium sulfate ( $[\text{NH}_4]_2\text{SO}_4$ ).

## EVOLUTION OF CHLORAMINATION CONTROL PRACTICES

Chloramine residual testing was conducted originally using the same methods used for free chlorine. The total residual was determined by iodometric titration. It wasn't until the use of orthotolidine that speciation of the various forms of residual chlorine could be determined. This led to improvements in the dosage control of both chlorine and ammonia. Subsequently, the development of amperometric differential titration led to an even better understanding of the chemistry of the chlorine residual compounds. Today DPD is the most common test indicator for chlorine residual analysis, and it is possible to use DPD to differentiate some chloramine compounds.

Improvements in ammonia testing have also been important to control excess ammonia and to verify optimum chlorine:ammonia feed ratios. The Nessler method was used as early as 1930 to analyze wastewater for ammonia. This method used the formation of iodine and its characteristic color to determine the concentration of ammonia. The phenate method provides an alternative when some interferences are present. The ammonia-selective electrode method, developed in the 1970s, has made the routine testing of ammonia in water possible.

## DISINFECTION REGULATIONS IN THE UNITED STATES

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In 1974, the United States passed the Safe Drinking Water Act (SDWA). Amendments were added in 1986 and again in subsequent years that set further criteria for acceptable levels of THMs (Connell 1996). The SDWA also encouraged alternate treatment methods to achieve the now twin goals of disinfection and minimized THMs.

The Disinfectants and Disinfection By-products Rule (USEPA 2001) established a maximum contaminant level (MCL) for THMs of 80 mg/L. The same rule set the MCL for HAAs at 60 mg/L. Maximum residual disinfectant levels were also set at 4.0 mg/L (ppm) for both chlorine and chloramine.

These regulations have caused utilities to carefully manage the use of chlorine. For example, the use of chlorine at the raw water intake is being reconsidered in favor of moving the point of addition closer to the clearwell. Intermediate points in the treatment plant would be considered on an as-needed basis. The addition of chlorine in conjunction with ammonia for use as the residual disinfectant in the distribution system is gaining popularity.

## INTERNATIONAL DISINFECTION REGULATIONS

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The World Health Organization (WHO) is a specialized agency of the United Nations. It publishes guidelines for drinking water quality that are used as a basis for the development of national drinking water standards. The 1998 guidelines include limits for disinfectants and disinfection by-products.

The European Union (EU) issued a directive (98/83/EC) that established minimum standards for water intended for human consumption. (More strict standards within the member states are allowed.) The directive includes disinfectants and disinfection by-product limits similar to the WHO guideline values.

The Netherlands has water systems operating without a residual in the distribution systems, indicating its great concern about the formation of THMs and other chlorinated by-products. The Netherlands' practices are not generally shared by the other European members. However, most of the practices of the EU states in the treatment of surface waters involve pretreatment with either ozone or chlorine dioxide, followed by chlorination of the finished waters.

Many countries have established their own drinking water quality standards. Most of these have adopted USEPA, EU, WHO, or a combination for their standards, yet the enforcement of standards varies widely from entirely voluntary to strict governmental oversight.

## THE FUTURE

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Chlorination practices will continue to be under scrutiny as more is learned about the effects of the disinfection process and the resulting disinfection by-products. Operation of surface water treatment plants and the quality of the water they produce will continue to be followed closely. Treated, potable water will continue to be examined in ever-increasing detail. New processes that will remove organic precursors will be discovered and used successfully.

Disinfection of drinking water is a vital component of the treatment and delivery system, and the protection of public health is the primary function of drinking water purveyors. It is a great challenge to provide microbiologically safe water and at the same time control disinfectant by-product production. Currently, scientific information is available to achieve these competing objectives. Further advancements, from scientific research, will undoubtedly lead the use of chlorine and chloramines in new directions in the future.

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