Abstract

Drinking water is a basic necessity for the maintenance of good health in humans, but it is also a vehicle for the introduction of harmful biological agents such as bacterial and protozoan pathogens into the body. Therefore raw waters are purified to render them safe for drinking. The processes adopted in municipal water purification include the following: pretreatment (pre-coagulation, pre-disinfection), aeration, coagulation, filtration (slow, rapid, ultrafiltration, carbon filtration), disinfection (chloramines, ozonation, ultraviolet light, chlorination) miscellaneous treatments (Fe/Mn removal, deionization, reverse osmosis, algal/odor control, softening, ion-exchange, fluoridation, radioactivity removal, plumbosolvency removal). Which of the processes is actually employed depends on the quality of the raw water, the regulations of the appropriate authorities, and the budgetary considerations of the operator. The world over, regulatory authorities decide the maximum contaminants permissible in drinking water and recreational water; thus, the US Environmental Protection Agency (USEPA), the European Union Environmental Agency (EEA), the World Health Organization (WHO), and governmental agencies around the world all set standards, which differ from one another, and which reflect the level of economic, social, and technical expectations and accomplishments of the constituencies to which the standards are addressed.

9.1 The Need for Water Purification

Water is a basic necessity of life and, as has been seen in the previous chapter, many diseases can easily be transmitted through it. The purification of water is the removal from raw waters, undesirable materials, whether biological or chemical in nature, so as to produce water that is fit for human consumption and for other uses. Substances that are removed during water purification include bacteria, viruses, algae, fungi, parasites (such as *Giardia* or *Cryptosporidium*), minerals (including toxic metals such as lead, copper, etc.), and man-made chemical pollutants. Some of the materials removed are detrimental to health, whereas others do

not necessarily affect health but affect the smell, taste, or color of water (Bitton 2005).

Governments the world over enact laws which ensure that water consumed by humans is safe to drink. In July 1970, the White House and Congress worked together to establish the US Environmental Protection Agency (EPA) in response to the growing public demand for cleaner water, air, and land. In the USA, the EPA works to develop and enforce regulations that implement environmental laws enacted by Congress. EPA is responsible for researching and setting national standards for a variety of environmental programs, and delegates to states and tribes the responsibility for issuing permits and for monitoring and enforcing compliance. Where national standards are not met, EPA can issue sanctions and take other steps to assist the states and tribes in reaching the desired levels of environmental quality.

In the European Union, the body which coordinates environmental matters is the European Environmental Agency (EEA), which has its headquarters in Copenhagen, Denmark. The Agency currently has 32 member countries: 27 European Union Member States, and 5 other cooperating non-EU countries.

The Ministry of the Environment of Japan was formed in 2001 from the subcabinet level Environmental Agency established in 1971. The minister is a member of the Cabinet and is chosen by the Prime Minister, usually from the Diet (Parliament).

Worldwide, in Africa, South America, and Asia, governments have either ministries or agencies handling the affairs of the environment, including water.

Much of the world's interest in the environment can be traced to the book, *Silent Spring*, published in 1962 and written by Rachel Carson. The book claimed detrimental effects of pesticides on the environment, particularly on birds. Carson accused the chemical industry of spreading disinformation, and public officials of accepting industry claims uncritically. It inspired widespread public concerns with pesticides and pollution of the environment. *Silent Spring* facilitated the ban of the pesticide DDT in 1972 in the United States.

Public water supplies are not only a source of drinking water, but are also for recreation; the processes of purification must reflect these uses (Anonymous 2006a, b). Therefore water is purified for the following reasons:

(a) To protect the health of the consumers by eliminating waterborne infections

(b) For aesthetic reasons, i.e., the removal of qualities which, while not being harmful, are aesthetically unpleasant. For example, the removal of taste, color, odor, and turbidity, all of which are not, in themselves, necessarily harmful to man

(c) For economic reasons, e.g., in softening water and removing iron to reduce laundry costs and save the laundered materials

(d) For industrial purposes, such as in the preparation of water suitable for use in boilers, e.g., by removal of salts of calcium and magnesium, which would form scales in boilers and increase heating costs and time

(e) For other miscellaneous reasons, e.g., to reduce corrosiveness and to add desirable health-related elements, e.g., iodine and fluorides to combat goiter and teeth decay, respectively

As seen from the above, an important requirement of water is the protection of health. This chapter will discuss the processes for purifying water so as to make it safe for consumption, to meet aesthetic expectations, and eliminate diseases transmitted through drinking water or recreational waters. It will discuss standards set by various bodies for the protection of health in drinking water, in the water used for recreation, and water in which shellfish are grown, because some shellfish are eaten raw (Tebbutt 1992).

9.2   The Quality of the Raw Water to Be Purified

Water treatment involves physical, chemical, and biological changes which transform raw waters into potable waters. The treatment to be employed has to be worked out from knowledge of the quality of the raw water and also the purpose for which the waters is needed. Thus, if drinking water is obtained from deep wells with low loads of bacteria, no treatment, apart from aeration, and not even chlorination, may sometimes be necessary. On the other hand, where the source is river or stream water, extensive purification including chlorination may be required. It is therefore essential that natural water supplies from which potable water is eventually obtained are not so polluted that self-purification and water treatment processes cannot produce water of reliable potability in an economical manner. In other words, the raw water must not be so highly polluted that the cost of purifying it puts it beyond the reach of the consumer. In many countries, therefore, governments enforce regulations to protect catchment areas, i.e., areas from which raw waters emanate.

The US Public Health Association has, e.g., classified raw waters into the following four categories:

Group I: Waters requiring no treatment

Limited to underground waters not subject to any possibility of contamination and meeting the standards of drinking water in every way.

Group II: Waters requiring simple chlorination

Includes underground and low contamination surface waters, containing 50 coliform bacteria per 100 ml per month.

Group III: Waters requiring complete rapid sand filtration and continuous post-chlorination

This group includes waters requiring filtration treatment for turbidity and color removal; waters requiring high amounts of chlorination, waters polluted by sewage to such an extent that they contain an average coliform numbers of 50–5.000 per 100 ml per month and beyond this number in not more than 20% of the samples examined in any month.

Group IV: Waters requiring auxiliary treatment as well as complete filtration treatment and post-chlorination

Similar to Group III, but showing coliform numbers more than 5.000 per 100 ml in more than 20% of the samples during any month and not exceeding 20.000 per 100 ml in more than 5% of the samples examined during any month. Auxiliary treatment includes pre-sedimentation with coagulation, pre-chlorination, or mere storage for extensive periods (30 or more days) (Anonymous 2006a).

Some authors argue that these standards are too low and hence should be revised to make them more stringent.

9.3 Processes for the Municipal Purification of Water

All or (more usually) some of the following treatments are given to raw waters to make them suitable for drinking (Singley et al. 2006).

1. Pretreatment
   (a) Pre-filtration
   (b) Pre-chlorination
   (c) pH adjustment
2. Storage and sedimentation without coagulation
3. Aeration
4. Coagulation and Flocculation
5. Sedimentation
6. Filtration
   (a) Slow sand
   (b) Rapid sand (with pre-coagulation and sedimentation)
   (c) Carbon filtration
   (d) Ultrafiltration
7. Disinfection
   (a) Chlorination
   (b) Chloramines
   (c) Ozonation
   (d) Ultraviolet
8. Iron and Manganese removal
9. Softening of water (sand stabilization) or demineralization
10. Fluoridation
11. Algae control (taste and odor control)
12. Miscellaneous treatments
    (a) Plumbosolvency removal
    (b) Radium removal
    (c) Reverse osmosis
    (d) Ion exchange
    (e) Electrodeionization

A flow diagram of the various processes in water treatment is given in Fig. 9.1. As many of the known procedures as possible are shown in the figure. Which procedure is actually used in any given situation depends on the quality of the raw water and how much consumers are willing to pay for the finished water. Thus, while the raw water from a surface water such as a river must be filtered either by rapid or by slow filtration in order the reduce the bacterial load, there would be no effort to achieve electrodeionization, since deionized water is required only in very specialized situations in laboratories. Therefore, various combinations of the basic procedures given above exist from plant to plant and in different countries .

9.3.1 Pretreatments

The pretreatments given to a body of raw water depend on the nature of the water and the practice of the plant or the country. What are described as pretreatments below are used as such in some works, but are major activities in others.

1. Pre-filtration
   To ensure the efficient and reliable operation of the main units in a treatment plant, it is first necessary to remove the large floating and suspended solids which could obstruct flow. This is especially true where the
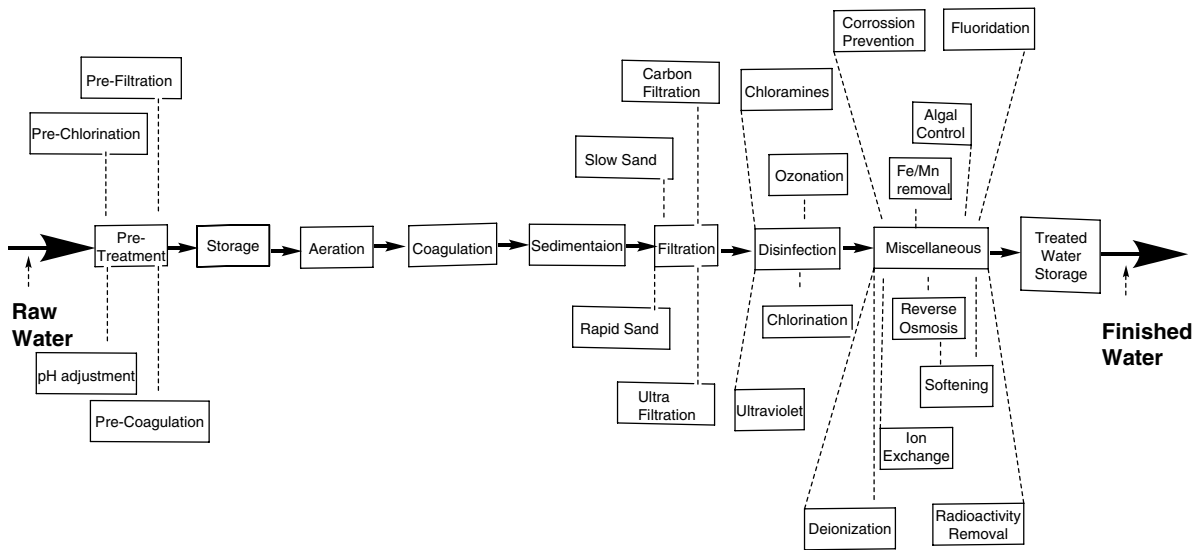
Fig. 9.1 Generalized methods for municipal purification of water

water supply is from surface waters such as rivers. The purpose is to remove large debris, including tree branches, rags, dead animals, fallen trees, etc., by passing the water through a 5–20 mm mesh.

2. Pre-chlorination

It is becoming more and more the practice to pre-chlorinate raw waters, especially in the case of surface waters such as river water. Pre-chlorination is said to increase the efficiency of the downstream processes, including the elimination of bacteria and the removal of taste and odor. Sometimes this is combined with pre-ozonation.

3. pH adjustment

If the water is acidic, the pH is raised using calcium oxide (lime, CaO). A slightly alkaline medium facilitates coagulation and flocculation. Furthermore, acid dissolves lead used in pipes, releasing it into the medium; lead is well known to have adverse health effects. The use of calcium could predispose the water to hardness; sodium carbonate is therefore often used in place of lime.

4. Pre-coagulation

Pre-coagulation is used when the raw water is very turbid

9.3.2   Storage and Sedimentation Without Coagulation

When raw waters are impounded, they are stored in reservoirs. Usually, no treatment is initially made on

such waters. They can be held for periods ranging from a few days to weeks or months. The mere fact of storage creates conditions favorable for the self-purification of the water through the activities of aerobic bacteria. Even the passage of water through a large lake will cause self-purification.

The factors of self-purification are interrelated and include physical, chemical, and biological factors and have been discussed in Chap. 7. They are, to a large extent, based on the activities of aerobic bacteria.

Sedimentation by gravity, if allowed to proceed for long enough, will remove all but the finest (colloidal) particles in the water (see Table 9.1).

Sunlight has a germicidal action in the upper 3 m (10 ft) in waters of low turbidity. Sunlight also induces photosynthesis in algae, thereby increasing the O_2 content of the water and hence the activity of the aerobes which break down organic matter. The oxidation of dissolved Mn^{++} and Fe^{++} compounds cause the oxides of these metals to precipitate. The breakdown of organic materials by aerobic bacteria is, however, the most important factor while the predatory activity of ciliates helps reduce the load of the bacteria themselves.

9.3.3   Aeration

Aeration is carried out in some waterworks but not in others. The purpose of aeration is as follows:

(a) To remove or reduce volatile taste, and odor, producing substances such as hydrogen sulfide,

Table 9.1 Sedimentation rate of objects of various diameters (Modified from Singley et al 2006)

Equivalent spherical radius	Approximate size	Sedimentation rate (time to settle 30 cm)
10 mm	Gravel	0.3 s
1 mm	Coarse sand	3 s
100 μm	Fine sand	38 s
10 μm	Silt	33 min
1 μm	Bacteria	55 h
100 nm	Colloid	230 h
10 nm	Colloid	6.3 years
1 nm	Colloid	63 years

methane, and other substances produced by bacteria or liberated by algal growth. Some taste- and odor-producing substances (such as geosmin produced by actinomycetes) are not volatile and are removed by other processes including coagulation and chlorination.

(b) To provide O_2 from the atmosphere for the oxidation of iron and manganese and thus to prevent corrosion and the staining of clothes.

(c) To restore "fresh" taste to water, as water devoid of dissolved air has a "flat" taste.

(d) In cases where water is obtained from very deep wells, where the water is hot, to cool the water.

During aeration, gases are dissolved by, or released from, the aerated water until an equilibrium is reached between the content of each individual gas in the atmosphere and its content in water. The diffusion of air into water is slow; hence, the need for agitation, which exposes various portions of the water to aeration. Since air normally contains little or no H_2S as well as other volatile gases, these are easily lost to the atmosphere during the aeration of water. On the other hand, when O_2 content is high because of algal activity, the excess O_2 is lost from water.

Temperature, as has been indicated earlier, also affects the amount of O_2 absorbed in water; the higher the temperature, the lower the O_2 dissolved.

Various designs of aerators are available; in some, water is allowed to fall by gravity over steps; in some, air is mechanically bubbled; in others, the water is forced into a fountain.

9.3.4 Coagulation and Flocculation

Coagulation and flocculation occur when colloidal particles clump together to such an extent that they settle out. Particles of the size of about 10-mm diameter will sediment unassisted in water, but smaller (or colloidal) particles will, for all practical purposes, not settle as shown in the Table 9.1. Because materials imparting color to water and a large proportion of the suspended materials in water are colloidal, they are best removed by coagulating them, hence causing them to sediment.
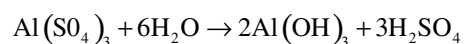
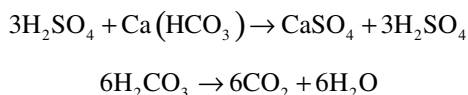Several methods may ordinarily be used to settle out colloids:

(a) *Aging* allows colloids to collide in quiescent water by Brownian movement and hence to coagulate, but the method is too slow.

(b) *Heating* increases the movement of the particles, causing them to collide more often and to settle out.

(c) The use of *antagonistic colloids* – i.e., colloids with opposite charges. However, in practical water treatment these other methods are not used; rather coagulants are used.

Coagulants are electrolytes which, in water, form gelatinous flocs and collect or absorb colloidal particles. As the weight of the flocs increase, sedimentation takes place. Many of the suspended water particles have a negative electrical charge. The charge keeps particles suspended because they repel similar particles. Coagulation works by eliminating the natural electrical charge of the suspended particles so they attract and stick to each other. The joining of the particles to form larger settleable particles called flocs is a process known as flocculation. The coagulation chemicals are added in a tank (often called a rapid mix tank or flash mixer), which typically has rotating paddles. In most treatment plants, the mixture remains in the tank for 10–30 s to ensure full mixing. The amount of coagulant that is added to the water varies widely according to the load of colloids.
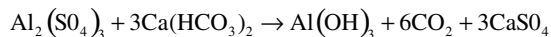
The coagulant is first rapidly mixed with water (in a *mixing basin)* to disperse it uniformly in water. It is next mixed at a slower rate by slow moving peddles to encourage flocculation or the massing of colloidal material and suspended particles. This takes place in a flocculation basin. The flocs sediment in special sedimentation tanks or clarifiers from which flocs are removed, intermittently or continuously.

The most popular coagulant used for water treatment is alum (aluminum sulfate). The reactions of alum in water are:

$$Al(S0_4)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2SO_4$$

$$3H_2SO_4 + Ca(HCO_3) \rightarrow CaSO_4 + 3H_2SO_4$$

$$6H_2CO_3 \rightarrow 6CO_2 + 6H_2O$$

Over all:

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow Al(OH)_3 + 6CO_2 + 3CaSO_4$$

For satisfactory coagulation, sufficient alkalinity must be available to react with the alum and also to leave a suitable residual alkalinity in the treated water.

The solubility of $Al(OH)_3$ is pH-dependent and is low at pH 5–7.5; in other words, for effective coagulation with alum, the pH of water should be in this range. Outside this range, coagulants sometimes used are ferrous sulfate $(FeSO_4)_3 \cdot 7H_2O$; also known as copperas, ferric sulfate $(Fe_2SO_4)_3$, ferric chloride $(FeCl_3)$, and sodium aluminate. Copperas may sometimes be treated with chlorine to give a mixture of ferric sulfate and ferric chloride known as chlorinated copperas. Ferric salts give satisfactory coagulation above pH 4.5 but ferrous salts are suitable only above pH 9.5. Iron salts are cheaper than alum but unless precipitation is complete, the former may stain clothes.

When colloidal matter is low, floc formation maybe encouraged by the addition of small amounts of coagulant aids, e.g., clay particles or, in some countries, heavy long-chain synthetic polymers.

These synthetic organic polymers ("polyelectrics") are long-chain carbon skeletons with recurring active sites, which absorb colloids. They have not come into general use, but are employed in some countries. Their advantages are that they are used in smaller volumes than the conventional coagulants, are simple to use because no pH maxima are involved, and they are cheaper and more efficient. Their disadvantages are that they require more vigorous mixing and also that they are yet to be as extensively studied as the better-known coagulants.

The amount of coagulants to be added has to be calculated from laboratory or jar tests. The pH of the raw water may be altered in the waterworks to suit the coagulant being used. The disposal of the sludge resulting from alum coagulation is sometimes a problem and in some countries, such as Japan, this is taken care of by various methods including lagooning (in which the sludge is allowed to settle in a lagoon and the supernatant recovered), drying beds, filter pressing, etc.

A method sometimes used is to draw about 10% of the clarified water, aerate it with air under pressure, and pump it to the bottom of the clarifying tank. The air bubbles float to the surface carrying with them the attached flocs. From time to time, this surface mat of flocs is scrapped and discarded. This method is called the dissolved air flotation method or DAF. Its advantage is that it reduces the load on the filters and is suitable for use with raw waters with a high amount of sediments.

9.3.5 Sedimentation

Water leaving the flocculation basin enters the sedimentation basin (settling basin or clarifier). Water flows through the tank slowly giving the flocs time to settle. It is usually a rectangle and so constructed that water flows through only at the top level. It typically takes 4 h for water to flow through a settling tank, but the longer the time in the sedimentation tank, the more the flocs that settle. The settling of flocs creates a bed of sludge, which could be between 2% and 5% of the total amount of water treated. The sludge must be removed from time to time.

9.3.6 Filtration

A minority of water personnel argue that if water is adequately stored and then chlorinated, it should be adequate for drinking. However, a great many waterworks still employ filtration (Anonymous 2007), of which there are two systems.

(a) Slow sand filtration

Filtration through sand was first developed in England, the earliest form having been used around 1829. The filters consist of 2–5 ft. of sand underlain by gravity. Particles in the raw water are filtered out near the top of the filter and provide a source of nutrients to microorganisms, which therefore grow to form a film. The slimy material formed by microorganisms, mud, and silt forms an efficient strainer.

After a period of use, depending on the nature of the raw water, the upper layers of the filter become clogged and have to be cleared by scraping. The sand may then be washed and reused. Slow sand filters can filter 3–6 million gal/acre/day. They

have the advantage that they are relatively simple, and do not require the expense of pre-coagulation. Second, because no coagulation is employed, the water is less corrosive and more uniform in quality. Finally, they are very efficient and 99.99% bacteria in water may be removed by a properly organized slow sand filter.

The disadvantages of the slow sand filter are that:

1. A large area is required and hence a large sand volume and consequent high initial costs are involved
2. Unless the raw water is allowed to reduce its load of suspended material by plain sedimentation, they are not very efficient for purifying turbid waters containing more than 30–50 ppm for prolonged periods.
3. They are not very effective in removing color.
4. Unless pretreatment is given, they give poor results due to clogging effect in waters of high algal content.

Ordinarily, slow sand filters are used without pretreatment. However, in some waterworks, all or some of these pretreatments may be given:

1. Sedimentation
2. Chlorination
3. Addition of $CuSO_4$ for algae removal

The in-flowing and out-flowing waters should be examined bacteriologically regularly to ensure that the filter is not clogged.

(b) Rapid sand filtration

Rapid sand filters were introduced in the USA in about 1893. Other synonyms of rapid sand filters are *mechanical filters* (since originally sand was mechanically agitated during washing), *pressure filters* (since sometimes filter units were enclosed in steel tanks and *pressure* applied), and *gravity filters* (since water flows by gravity). They were introduced in the attempt to increase the rate of filtration to a calculated optimum of 125 million gal water /acre per day (2 gal/sq. ft/per min). The water to be filtered at this rate had to undergo prior coagulation and sedimentation to remove colloidal materials, which would otherwise block the filter. The present-day rapid sand filtration procedure consists of coagulation, flocculation, and sedimentation (discussed earlier), followed by filtration.

The rapid sand filter is a tank or box containing 20–30 in. of filter sand of 0.35–0.45 mm diameter overlying 16–24 in. of gravel ranging in diameter from 1/8 to 2½ in. The gravel is usually arranged in three to five layers, each layer containing material twice the size of that above it. The underdrain system collects the water for distribution and consists of perforated pipes with brass strainers. The coagulated water which at this stage carries a turbidity of about 10 ppm is distributed uniformly on the filter bed. Suspended material carried over from the sedimentation tanks as well as silt, clay, algae, and bacteria soon clog the filters and such materials are washed out in the flushing action of a back current of water, operated at about ten times the rate of filtration of the water. Sometimes the filter beds may be made of anthracite coal particles instead of sand.

To clean the filter, water is passed quickly upward through the filter, opposite the normal direction (called *backflushing* or *backwashing*) to remove embedded particles. Prior to this, compressed air may be blown up through the bottom of the filter to break up the compacted filter media to aid the backwashing process. Plate counts for bacteria should be done regularly before and after filtration to check the efficiency of the filter. Some plants use a slow sand filter after the rapid sand.

9.3.7   Chlorination (and Other Methods of) Disinfection

Even after the various treatments given to water – aeration, coagulation, sedimentation, and filtration – the possibility still exists that water may contain some bacteria, hence the need for disinfection. It should be noted, however, that complete sterilization is not aimed at in water treatment, even if it were possible to achieve this.

A number of chemicals have been used for the disinfection of water. The most common and most widely used are chlorine and its compounds, e.g., chloride of lime or calcium hypochlorite.

Historically, the introduction of the use of chlorine for disinfecting water has been credited to Sir Alexander H. Houston, who has also been called the "Father of Chlorination." He and a Dr. McGowan in 1904–1905 began the first continuous chlorination process designed to disinfect the municipal water supply of the city of Lincoln, England. They had used a 10–15% sodium hypochlorite solution for the purpose. Prior to

Table 9.2 Usage of chlorine as a water disinfectant in comparison with others (From The American Chemistry Council. http://www.americanchemistry.com/s_chlorine/sec_content.asp?CID=1133&DID=4530&CTYPEID=109.   With   permission) (Anonymous 2010a)

Disinfection	Large systems (>10,000 persons)	Small systems (<10,000 persons)
Chlorine gas	84%	61%
Sodium hypochlorite	20	34
Calcium hypochlorite	<1	5
Chloramines	29	–
Ozone	6	–
UV	–	–
Chlorine dioxide	8	–

that, between 1824 and 1826, chlorine had been introduced into hospitals, especially in obstetrical wards for the prevention of puerperal fever. A little later, in about 1831, it had been used in water (but not on a continuous scale) during the great cholera epidemic in Europe. Today, most water disinfection around the world is done with chlorine (see Table 9.2).

Chlorine has a number of advantages:

(a) It is easily available as a gas (or in compounds as liquid or powder).
(b) It is reasonably cheap.
(c) It is highly soluble (700 mg/l).
(d) It leaves a residue in solution which, while not harmful to man, provides protection in the distribution system.
(e) It is highly toxic to microorganisms.
(f) It has several important secondary uses, e.g., oxidation of iron, manganese, and H_2S, destruction of some taste- and odor-producing compounds, and acts as an aid to coagulation.

However, some of its shortcomings must be borne in mind:

(a) It is a poisonous gas and must be carefully handled.
(b) It can itself give rise to taste and odor problems, particularly in the presence of phenol (hence ammonia was once added to form chloramines, which have less odor problems).
(c) Suspended materials may shield bacteria from the action of chlorine.
(d) Chlorine is a powerful oxidizing agent and will attack a wide range of compounds, including unsaturated organic compounds as well as reduce substances, which are found in water, thereby making it less available to attack microorganisms.

(e) The effectiveness of chlorination is pH-dependent; chlorination is more effective at pH values of 7.2 and below than above pH 7.6.

There are alternative methods of disinfecting water and they are compared with chlorine in Table 9.3.
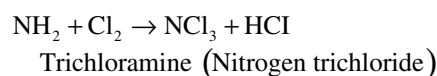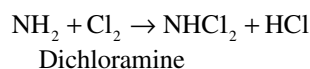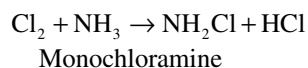
9.3.7.1 Reactions of Chlorine with Chemicals Found in Water

When water is chlorinated, a large number of chemicals may be present in it, especially if the water is wastewater or effluents from sewage treatments. These chemicals include nitrogenous compounds (especially ammonia), carbonaceous compounds, nitrites, iron, manganese, hydrogen sulfide, and cyanides. Chlorine combines with many of these compounds in the following manner.

(a) Nitrogen containing compounds

The compounds formed by the reaction of chlorine and a nitrogen-containing compound are chloramines, which could be either inorganic or organic.

1. *Ammonia*: This is the most important inorganic compound, which reacts with chlorine; others are nitrates and nitrites. Chlorine reacts in dilute aqueous solutions (1–50 ppm.) to form three choramines:

$$Cl_2 + NH_3 \rightarrow NH_2Cl + HCl$$
Monochloramine

$$NH_2 + Cl_2 \rightarrow NHCl_2 + HCl$$
Dichloramine

$$NH_2 + Cl_2 \rightarrow NCl_3 + HCI$$
Trichloramine (Nitrogen trichloride)

These chloramines, also known as combined residuals, have disinfectant properties, but they are far less effective than chlorine, requiring about ten times the contact time of chlorine. Furthermore, they confer odor and taste to water.

The pH of the water determines the relative amounts of the three kinds of chloramines. At pH 8.5, monochloramine is the major product. If it is low, e.g., below pH 4.4, virtually all the chloramine is in the form of nitrogen trichloride (NCl_3), which imparts a bad taste to drinking water and causes eye irritation in swimming pools. At the same time, it hardly disinfects.

Table 9.3 Comparison of chlorine and other water disinfectants (From The American Chemistry Council. http://www.americanchemistry.com/s_chlorine/sec_content.asp?CID=1133&DID=4530&CTYPEID=109. With permission) (Anonymous 2010c)

Disinfectant	Advantages	Limitations
Chlorine Gas	• Highly effective against most pathogens • Provides "residual" protection required for drinking water • Operationally, the most reliable • Generally the most cost-effective option	• By-product formation (THMs, HAAs[a]) • Special operator training needed • Additional regulatory requirements (EPA's Risk Management Program) • Not effective against Cryptosporidium
Sodium hypochlorite	• Same efficacy and residual protection as chlorine gas • Fewer training requirements than chlorine gas • Fewer regulations than chlorine gas	• Limited shelf life • Same by-products as chlorine gas, plus bromate and chlorate • Higher chemical costs than chlorine gas • Corrosive; requires special handling
Calcium hypochlorite	• Same efficacy and residual protection as gas • Much more stable than sodium hypochlorite, allowing long-term storage • Fewer Safety Regulations	• Same byproducts as chlorine gas • Higher chemical costs than chlorine gas • Fire or explosive hazard if handled improperly
Chloramines	• Reduced formation of THMs, HAAs • More stable residual than chlorine • Excellent secondary disinfectant	• Weaker disinfectant than chlorine • Requires shipment and use of ammonia gas or compounds • Toxic for kidney dialysis patients and tropical fish
Ozone	• Produces no chlorinated THMs, HAAs Fewer safety regulations • Effective against Cryptosporidium • Provides better taste and odor control than chlorination	• More complicated than chlorine or UV systems • No residual protection for drinking water • Hazardous gas requires special handling • By-product formation (bromate, brominated organics and ketones) • Generally higher cost than chlorine
UV	• No chemical generation, storage, or handling • Effective against Cryptosporidium • No known by-products at levels of concern	• No residual protection for drinking water • Less effective in turbid water • No taste and odor control • Generally higher cost than chlorine
Chlorine dioxide	• Effective against Cryptosporidium • No formation of THMs, HAAs • Provides better taste and odor control than chlorination	• By-product Formation (chlorite, chlorate) • Requires on-site generation equipment and handling of chemicals • Generally higher cost than chlorine

[a] *THMs* trihalomethanes, *Haas* haloacetic acids

2. *Organic nitrogen*: Organic nitrogen compounds include proteins and its various breakdown products – peptones, polypeptides, and amino acids. These compounds greatly retard chlorine with which they may react over several days. Known as chloro-organic compounds, they contribute to the odors in water. Furthermore, they produce a series of unstable residuals. Chloro-organic compounds, which titrate as combined chlorine, are also believed to have no germicidal action. Apart from all these, organic nitrogen is undesirable because it is a fairly good indication of recent pollution. It has therefore been suggested that its amount in raw waters be limited to 0.3 mg/1. The smaller the amount of protein, the more available chlorine is for disinfection.

(b) Hydrogen sulfide

H_2S is frequently dissolves in underground water and is common in waters where anaerobic decomposition has occurred. At a pH value of 6.4 and below, the H_2S is completely oxidized, giving rise to sulfuric acid and hydrochloric acid:

$$H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$$
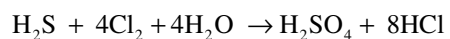
At higher pH values, the reaction is thus

$$H_2S + Cl_2 \rightarrow S + H_2O$$
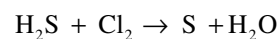
(c) Iron

The precipitate resulting from the reaction of chlorine and iron (i.e., $Fe(OH)_2$) in water serves two useful purposes. First, it helps remove iron; second, it helps produce a coagulant for the treatment of the water. The ultimate reaction is thus:
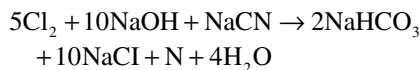
$$2FeCl_3 + 3Ca(HCO_3)2 \rightarrow 2Fe(OH)3$$
$$+ 6CO_2 + 3CaCl_2$$
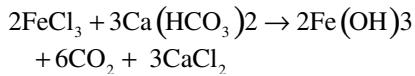
(d) Cyanide

The destruction of cyanide by chlorine is most effective at high pH values (8.5–9.5), which can be created when necessary by the addition of NaOH. Sodium cyanate is produced, which decomposes, releasing nitrogen.
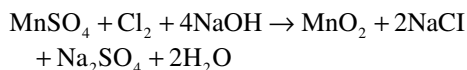
$$2Cl_2 + 4NaOH + 2NaCN \rightarrow 2NaCNO + 4NaCl$$
$$+ 2H_2O \qquad \text{(sodium cyanate)}$$
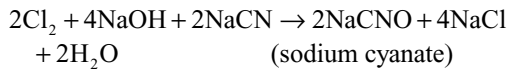
The complete reaction is thus:

$$5Cl_2 + 10NaOH + NaCN \rightarrow 2NaHCO_3$$
$$+ 10NaCI + N + 4H_2O$$

(e) Manganese

Chlorine reacts with manganese at pH 7–10, thus

$$MnSO_4 + Cl_2 + 4NaOH \rightarrow MnO_2 + 2NaCI$$
$$+ Na_2SO_4 + 2H_2O$$

(f) Methane

Methane is produced by anaerobic bacteria. Besides its unpleasant odor, methane could be explosive. It is best removed by aeration, but chlorine also reacts with it.

$$2CH_4 + Cl_2 + H_2O \rightarrow 4HCl + H_2O$$

9.3.7.2 The Present Practice of Water Chlorination

The current practice of chlorination is to add sufficient chlorine to oxidize all organic matter, iron, manganese, and other reducing substances in water as well as oxidize free ammonia in raw waters, and leave unused chlorine as free residual chlorine rather than the less active combined residual chlorine or chloramines. The process is known as "super-chlorination," "break-point chlorination," or "free residual chlorination" (see Fig. 9.2).

The reactions of chlorine with progressively large doses of chlorine are shown in Fig. 8.2. Free residual chlorine is not molecular chlorine reacting as a dissolved gas except at pH values below 5. When chlorine is dissolved in water, it dissociates to form two germicidal compounds, hypochlorous acid (HOCI) and the chlorite ion (OCI). The undissociated molecule of hypochlorite ion is 100 times more germicidal than the chlorite ion. At pH 5.6, the chlorine forms hypochlorous and hypochloric acid, thus:

$$Cl_2 + H_2O \rightarrow HCl + HClO$$

Free residual chlorine

$$HClO \rightarrow H + ClO$$
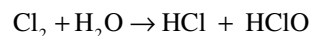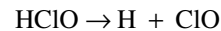
In earlier chlorination practice, only 0.1–0.2 ppm. of chlorine was added. The result was that though there
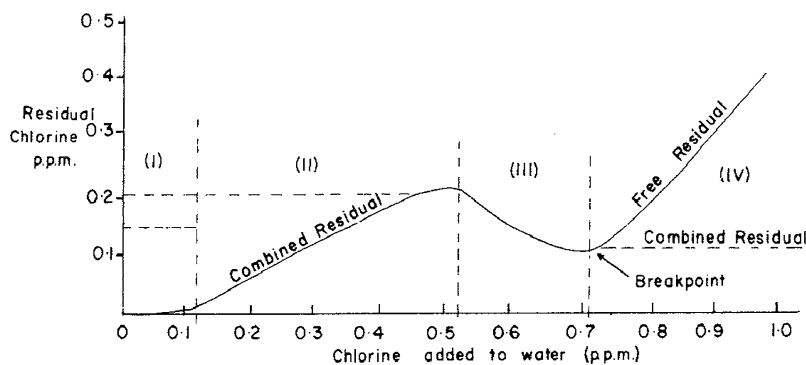
I = **Destruction of chlorine by reducing compounds; no residual chlorine and no disinfection**

II = **Formation of chloro-organic compound and chloramines, used in earlier chlorination practice**

III = **Destruction of chloramines and chloro-organic compounds; breakpoint zone; chloramines oxidized.**

IV = **Formation of free chlorine and presence of presence of undestroyed chloro-organic compounds**

Fig. 9.2 Modern (breakpoint) chlorination (Modified from Tebbutt 1992; http://water.me.vccs.edu/concepts/chlorchemistry.html) (Anonymous 2010b)

was residual chlorine, it was combined residual chorine in chloro-organic compounds and chloramines. These were not only less effective as disinfectants but also possessed odor and/or taste.

Undissociated hypochlorous acid is far more effective as an antimicrobial agent than the chlorite ion. Between pH 6 and pH 8.5–9, the hypochlorous acid is in equilibrium with the chlorite. Nearer the upper limit, nearly all (about 90%) of the hypochlorous acid is ionized to chlorite ion, whereas at about pH 6, it is mainly hypochlorous acid (see Table 9.2). Fortunately, most waters have a pH of 6.0–7.5, hence 50–95% of the free residual chlorine is present as hypochlorous acid. Many methods of chlorine determination in water unfortunately merely measure combined $HOCl + OCl$; the pH of the water must be known if the amount $HOCl$ is to be known.

9.3.7.3 Mode of Action of Chlorine Disinfection

It should be explained that chlorine in water does not *sterilize* (i.e., it does not remove all forms of living things). It merely disinfects (i.e., it destroys pathogenic organisms, much as the mild heat treatment of pasteurization does). Complete sterilization would be impractical because of its expense and is, in any case, not necessary.

The germicidal action of chlorine was first believed to be entirely due to the liberation of nascent oxygen by the reaction:

$$HOCl \rightarrow HCl + O$$
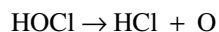
This was dispelled when it was shown that nascent oxygen was not released. It is now accepted that the disinfectant is hypochlorous acid, which has a small neutral molecule shaped like water and hence easily diffuses into the cell. The negative charge of the OCl ion, on the other hand, hampers its own penetration into the cell. The sites of action of the hypochlorous acid are the sulfhydryl (−SH) groups of enzymes.

9.3.7.4 Factors Affecting the Efficacy of Disinfection in Water by Chlorine (and the other Halogens)

Some of the factors affecting the efficacy of chlorine as a disinfectant in water are the type of organisms, the number of each organism, the concentration of chlorine, the contact time, the temperature, and the pH.

1. Type of organism
   Organisms vary in their resistance to killing by chlorine. In general, the order (of decreasing resistance) is: bacterial spores, protozoan cysts, viruses, and vegetative bacteria. Diseases produced by spore formers, e.g., anthrax *(B. anthracis)*, bolutilism *(Cl. botulimum)*, and tetanus *(Cl. tetanus)* are not normally transmitted via water although their spores may be transported therein. *Cl welchii,* an inhabitant of man's alimentary canal, is also sometimes used as an indicator of fecal contamination. It seems reasonable, therefore, for the spore formers to be used as test organisms for disinfection because of their greater resistance than *E. coli* and other non-sporulating bacteria. They have however not been used up till the present time.

   Cysts of the pathogenic protozoa *Entamoeba histolytica* and *Giardia lambia* are shed in feces of affected patients. Because the cysts are highly impermeable, they are said to be about 160 and 90 times more resistant than *E. coli* and hardier than enteroviruses, respectively, to hypochlorous acid.

   Chlorination as currently practiced does not remove all viruses from water and many of them persist after vegetative bacteria in water have been eliminated. Viruses, which are waterborne, have been discussed in Chap. 8. Table 9.3 compares the effectiveness of various disinfecting agents used in water.

2. The number of organisms, the concentration of chlorine, and the contact time
   As with other disinfecting agents, the greater the number of organisms the greater the concentration of chlorine required to kill a given number of organisms in a given time. In practice, the minimum contact time is 10–15 min.

3. Temperature
   The higher the temperature, the lower the rate of dissolution of chlorine or any gas. However, higher temperature affects the dissolved chlorine in two ways. First, it increases the rate of chlorine reactions with ammonia. Second, it affects the germicidal power of free residual chlorine. Thus, a 99.6–100% kill of the coxsackie A2 virus will require 4 min at pH 7 at 0–5°C, and 2 mg/l free residual chlorine; at 20–29°C it will require only 0.2 mg/l. residual chlorine – about tenfold reduction of chlorine. This emphasizes the need for recalculating the chlorine concentration

required for effective kills in outdoor disinfection in tropical countries, when the only data available are from temperate countries.

4. pH

The acidity of water affects the dissociation of HOCl. At lower pH values, HOCl predominates and at higher pH values the OCl (hyprochorite) ion whose disinfecting ability is low, predominates. A well-defined equilibrium will be established at various pH values for each of the hypohalous acids, thus:

$$HOA \leftrightarrow H^+ + OX^-$$
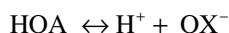
When bromine is used, there is a preponderance of the more bactericidal hypobromous acid, HOBr, when the pH of the water is less than 8.7. With chlorine, HOCl predominates at pH less than about 7.45. Iodine is unusual because at the usual pH of water (5–8), there is hypoiodite ion, and the iodine exists mainly as molecular iodine I_2, and hypoiodous acid, HIO or H_2IO^+:

$$I_2 + H_2O \leftrightarrow H_2OI^+ + I^-$$

Iodine further differs in that whereas chlorine and bromine form chloramines and bromanines when ammonia is present in the water, iodine does not form iodamines with NH_3, nor does it react readily with organic matter. Iodine can however be discounted as a means of disinfecting water because it is physiologically active and may affect the thyroid. Apart from this, it is expensive. Iodine has however been shown to be quite suitable for use in swimming pools. In this connection, its lack of reactivity in water with ammonia and organic matter over a wide range of pH values is an advantage. It is thus able to remain in water as the molecular form I_2.

Bromine is also active, but it is expensive to produce; besides, it will require acclimatization by both water handlers and consumers to adapt to its use. There seems, therefore, to be no compelling reason to change to its use. Certain compounds of the halogens, chlorine, and bromine, may also be used. Notable among these are the compounds resulting from their reaction with ammonia, but these are generally less active than the hypohalous

acids. Still, other compounds, bromine chlorine, and chlorine dioxide, have been tried mainly in wastewater.

The disinfecting activity of chlorine and its compounds, as well as ozone and uv are compared in Table 9.3. The table shows that while chlorine and its compounds are efficient disinfectants they are limited by their ineffectiveness, unlike ozone and uv, against protozoan cysts (Cryptosporidium).

9.3.7.5 Tests for Chlorine in Water

Chlorine in water reacts to form either free residual chlorine (HOCl + OCr) or combined residual chlorine (chloramines and chloro-organic compounds). These chlorine compounds are oxidizing to varying extents and this variability is the basis of chlorine tests in water. The tests are (a) the orthotolidine method (b) the starch – iodine method (c) amperometric method, and (d) titration with ferrous ammonium sulfate.

In the *orthotolidine* method, the free residual chlorine reacts in a matter of seconds with the colorless orthotolidine (a benzidine structure) to form a highly colored yellow holoquinone at low pH, thus:
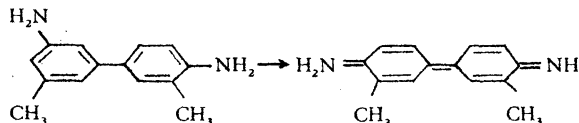
The combined residual chlorine reacts much more slowly and can be removed with arsenite after the free chlorine has reacted. The yellow color can then be compared with a standard.

The *starch–iodine* method depends on the reaction:

$$HOCl + 2I + H+ \rightarrow I_2 + Cl + H_2O$$
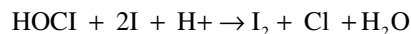
This iodine is titrated with starch. The method is not very useful with drinking water and is more applicable with wastewater where all the chlorine is usually combined.

In the *amperometric* method, two platinum electrodes are immersed in a sample and a voltage of 10–15 mV applied. The reaction $HOCl + H + I_2 + Cl + H_2O$ also takes place. Iodine is oxidized at the anode and reduced at the cathode, thus causing current to flow. Changes in

iodine concentration produce changes in current, which can be recorded. In water, it is useful in distinguishing free from residual chlorine. By altering the pH, the various combined residuals can be determined.

In the *titration with ferrous ammonium sulfate*, the titrating agents (e.g., sodium hexametaphosphate) react with chlorine at pH 7 to give a clear color when chlorine residual is present. Iodine is added and the addition of blue color is titrated and measured as monochloramine. Acidity after this neutralization to the original pH gives the dichloraning content on titration.

The most widely used of these methods is the ortho-tolidine–arsenite method, but it has been discontinued in some countries because the indicator is believed to be carcinogenic.

9.3.7.6 Alternative Methods of Disinfection Besides Chlorine and Other Halogens

Chlorine is an excellent water disinfectant whose advantages and disadvantages have already been discussed earlier in this chapter. Some work has gone into trying to find substitutes for chlorine. The reasons for this search are as follows. First, natural organic compounds in water, including humic acids, react with chlorine to produce volatile and nonvolatile halogenated compounds. The result is that the finished water contains a greater amount of these undesirable chloro-organic compounds than the raw water. For example, chloroform has been found to be less than 1 mg/l in raw water, but more than 300 mg/l after chlorination. Other compounds besides chloroform found in chlorinated water beside chloroform are carbon tetrachloride and 1,2-dichloroethane. These compounds confer unpleasant odors to water. The second reason for the search for other disinfection methods is that many viruses are known to be more resistant than *E. coli*. Hence, the absence of *E. coli* does not absolve a water sample from being a possible source of infection. The alternatives which have been considered outside the halogens are, in some cases being used, ozone and ultraviolet light (Weintraub et al 2005).

9.3.7.7 Ozone

Ozone, O_3, is produced on-site by introducing high voltage electric discharge (6–20 kV) across a dielectric discharge gap that contains oxygen-bearing gas.

Ozone is produced when oxygen (O_2) molecules are dissociated by an energy source into oxygen atoms; these subsequently collide with an oxygen molecule to form an unstable gas, ozone (O_3).

It is used in some European countries, notably France and Switzerland, for water disinfection. In the US, it is sometimes used to treat water discharged from wastewater treatment plants. Because of its powerful oxidizing properties, it is also used for removal of odor and taste, manganese, and organic compounds.

1. Advantages of ozone for water disinfection:
   The advantages of ozone are as follows:
   (a) Ozone is more effective than chlorine in destroying viruses and bacteria; it is highly virucidal while being at least as bactericidal as chlorine.
   (b) Ozone's germicidal action is extremely rapid – acting sometimes in a matter of seconds (see Fig. 8.4). However, in practice, the contact period allowed for efficient killing, depends on the turbidity of the water. Thus, for a 5–10 min period used in practice, 0.25–0.5 mg/l turbidity has been recommended for good-quality ground water. Owing to its rapidity of action, and to accommodate differences in the quality of the raw water, many plants adopt a general procedure of approximately 10–30 min for contact when treating waters with ozone.
   (c) There are no harmful residuals that need to be removed after ozonation because ozone decomposes rapidly.
   (d) After ozonation, there is no regrowth of microorganisms, except for those protected by the particulates in the wastewater stream.
   (e) Ozone is generated on-site, and thus, there are fewer safety problems associated with shipping and handling.
   (f) Ozonation elevates the dissolved oxygen (DO) concentration of the effluent. The increase in DO can eliminate the need for re-aeration and also raise the level of DO in the receiving stream.
   (g) Its efficacy is not affected by pH in the range (pH 5–8), and turbidity of up to 5 mg/l does not affect it.

2. Disadvantages of ozone: Ozone, however, has the following disadvantages:
   (a) Low dosages may not effectively inactivate some viruses, spores, and cysts.

(b) Ozonation is a more complex technology than is chlorine or UV disinfection, requiring complicated equipment and efficient contacting systems.

(c) Ozone is very reactive and corrosive, thus requiring corrosion-resistant material, such as stainless steel.

(d) Ozonation is not economical for water with high levels of suspended solids (SS), biochemical oxygen demand (BOD), chemical oxygen demand, or total organic carbon.

(e) Ozone is extremely irritating and possibly toxic, so off-gases from the contactor must be destroyed to prevent worker exposure.

(f) The cost of treatment can be relatively high, being both capital- and power-intensive.

(g) There is no measurable residual to indicate the efficacy of ozone disinfection. It is for this reason that post-ozonation chlorination is practiced in some countries.

Factors affecting the Efficacy of Ozonation in Water

1. *Temperature*

   Temperature has an important influence on the half-life of ozone (i.e., time it takes for it to disintegrate). Table 9.4 shows the half-life of ozone in air and water. In water, the half-life of ozone is much shorter than in air; in other words, ozone decomposes faster in water. The solubility of ozone decreases at higher temperatures and is less stable. On the other hand, the reaction speed increases by a factor 2 or 3 per 10°C. Principally, ozone dissolved in water cannot be applied when temperatures are above 40°C, because at this temperature, the half-life of ozone is very short (Table 9.4).

2. *pH*

   Ozone decomposes partly into OH⁻ radicals. When the pH value increases, the formation of OH⁻ radicals increases. In a solution with a high pH value, there are more hydroxide ions present, see formulas below. These hydroxide ions act as an initiator for the decay of ozone:

   $$O_3 + OH^- \rightarrow HO_2^- + O_2 \tag{9.1}$$

   $$O_3 + HO_2 - \rightarrow \ ^\bullet OH + O_2^{\bullet -} + O_2 \tag{9.2}$$
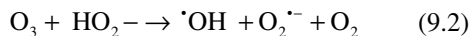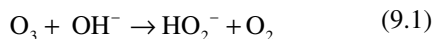
   The radicals that are produced during reaction 2 can introduce other reactions with ozone, causing more

Table 9.4 Half-life of ozone in gas and water at different temperatures (From Lenntech Delft the Netherlands. http://www.lenntech.com/library/ozone/decomposition/ozone-decomposition.htm. With permission) (Anonymous 2009a)

Air		Dissolved in water, pH 7	
Temp (°C)	Half-life	Temp (°C)	Half-life
−50	3 months	15	30 min
−35	18 days	20	20 min
−25	8 days	25	15 min
20	3 days	30	12 min
120	1.5 h	35	8 min
250	1.5 s		

OH-radicals to be formed. The decay of ozone in a basic environment is much faster than in an acid environment.

3. *Dissolved solids concentration*

   Dissolved ozone can react with a variety of matter, such as organic compounds, viruses, bacteria, etc. They react with ozone in different ways, causing ozone to break down to the OH- ion. Some dissolved compounds hasten the breakdown of ozone into the OH ion, while some delay the breakdown. Those which react with the OH ion and slow down the breakdown are referred to as scavengers. For example, carbonates are strong scavengers. The addition of the carbonate ion increases the half-life of ozone.

4. *Dissolved organic matter (DOM)*

   Dissolved organic matter (DOM), also called dissolved organic carbon (DOC), is present in every kind of water. It is largely colloidal in nature; the materials, which confer color and odor in water, are colloidal and part of the DOM in water. Ozone is used to reduce DOC in water and hence color and odor. Ozone easily reacts with reactive chemical structures such as double bonds, activated aromatic compounds, amines, and sulfides. The OH- ion also directs with DOM.

Mode of Action of Ozone

When ozone decomposes in water, the free radicals hydrogen peroxy (HO_2) and hydroxyl (OH) that are formed have great oxidizing capacity and play an active role in the disinfection process. It is generally believed that the bacteria are destroyed because of protoplasmic oxidation resulting in cell wall disintegration (cell lysis). The effectiveness of disinfection depends on the susceptibility of the target organisms, the contact time, and the concentration of the ozone.

Ozone is a very strong oxidant microbicide and virucide. The mechanisms of disinfection using ozone include:

(a) Direct oxidation/destruction of the cell wall with leakage of cellular constituents outside of the cell.

(b) Reactions with radical by-products of ozone decomposition.

(c) Damage to the constituents of the nucleic acids (purines and pyrimidines).

(d) Breakage of carbon–nitrogen bonds in nucleic acids leading to depolymerization.

9.3.8 Ultraviolet Light

Special lamps are used to generate the radiation that creates UV light by striking an electric arc through low-pressure mercury vapor; a broad spectrum of radiation with intense peaks at UV wavelengths of 253.7 nm (nm) and a lesser peak at 184.9. The germicidal UV range exists between 250 and 270 nm. At shorter wavelengths (e.g., 185 nm), UV light is powerful enough to produce ozone, hydroxyl, and other free radicals that destroy bacteria.

Using ultraviolet (UV) light for drinking water disinfection dates back to 1916 in the U.S. UV costs have since declined as new UV methods to disinfect water and wastewater have been developed (Anonymous 2007). Currently, several states have developed regulations that allow systems to disinfect their drinking water supplies with UV light. The US Environmental Protection Agency (EPA) lists UV disinfection as an approved technology for small public water systems. The use of UV for disinfecting water and wastewater has advantages and disadvantages.

1. Advantages of UV for disinfecting water
   The advantages include:
   (a) UV has no known toxic or significant nontoxic byproducts.
   (b) It has no danger of overdosing.
   (c) With UV, there are no volatile organic compound (VOC) emissions or toxic air emissions.
   (d) No on-site smell and no smell in the final water product exist with UV.
   (e) Contact time with UV is very short; it occurs in seconds, but in minutes for chemical disinfectants.
   (f) UV requires very little space for equipment and contact chamber.

(g) It improves the taste of water because some organic contaminants and nuisance

(h) UV does not react

(i) Has little or no impact on the environment.

2. Disadvantages of water disinfection using UV
   The use of UV has the following disadvantages:
   (a) UV radiation is not suitable for water with high levels of suspended solids, turbidity, color, or soluble organic matter; they react with UV radiation, and reduce disinfection
   (b) performance. In particular, high turbidity makes it difficult for radiation to penetrate water.
   (c) In comparison with chlorine, it has no disinfection residual.
   (d) Using ultraviolet light on a large scale is a more expensive process than the use of chemicals.

9.3.8.1 Mode of Action and Use of UV

Ultraviolet light kills microorganisms by causing the coalescing or dimerization of adjacent thymine bases in the DNA of organisms exposed to it. It has its maximum germicidal effect at 2,500–2,600 A wavelength (250.0–260.0 nm).

The major feature of the set-up for UV water sterilization is that water circulates round a chamber in which ultraviolet lamps are located. According to the U. S. Dept. of Health, Education & Welfare, Public Health Service, the retention time of water in the chamber should not be less than 15 s, at the maximum flow rate of the system. The flow rate must not exceed 0.0125 m^3/s per effective (arc length) inch of the lamp. The lamp must also emit light energy at 253.7 nm at an intensity of 4.85 UVW/sq. ft (0.005 UVW /sq. cm) at a distance of 2 m (see Fig. 10.23).

9.3.9 Iron and Manganese Control

Iron and manganese either together or alone are objectionable in water because beyond certain levels they stain clothes and they may give an unwelcome deposit in drinking water. They can make water appear red or yellow, create brown or black stains in the sink, and give off an easily detectable metallic taste. They can be aesthetically displeasing, but iron and manganese do not constitute health risks.

These minerals are to be found in waters obtained from certain deep waters, which contain CO_2 but

not O_2 Under these conditions, the insoluble oxides of these metals are reduced and transformed to soluble carbonates. It is possible to determine the source of the staining or other observations resulting from the presence of iron in water, thus:

(a) When the water is clear but has rust or black-colored particles, then it is due to ferrous iron – Fe^{2+}.

(b) When the water from the tap is red, yellow, or rusty and sediments soon form on resting, then the culprit is ferric iron, Fe^{3+}.

(c) When in metallic pipes, slimy brown, red, or green masses on the pipes appear, this is diagnostic of iron bacteria.

Iron and manganese may be removed in any of the following ways:

1. Aeration:
   This introduces oxygen and hence causes oxidation and precipitation of oxides.

2. Use of contact bed containing iron and manganese oxides
   Water is passed over a bed of gravels coated with Fe and Mn oxides. These oxides enhance oxidation of Fe and Mn through catalytic action of preciously precipitated oxides. Contact beds are regenerated potassium permanganate $KMnO_4$.

3. Oxidation by Chlorine or $KMnO_4$
   Appropriate amounts of free residual chlorine will oxidize Fe and Mn. It is usually aided by a small amount at $CuSO_4$. Potassium permanganate may also be used.

9.3.10 Softening of Water

Hard water is water that has a high soap consuming power (i.e., water which will not produce lather unless a large amount of soap is used). Besides soap wastage, hard water also forms sediments or scales in kettles, industrial boilers, thereby requiring more heat for the same amount of water. Hard water also contributes to skin clogging and discoloration of porcelain, and shortening of the life of fabrics. Hardness in water is due primarily to the presence of Ca and Mg ions. The presence of the following may also cause slight increases in hardness: Fe, Mn, Cu, Ba, and Zn.

Total water "hardness" (including both Ca^{2+} and Mg^{2+} ions) is reported as ppm w/v (or mg/L) of $CaCO_3$. Water hardness usually measures the total concentration of Ca and Mg, the two most prevalent divalent metal ions, although in some geographical locations,

iron and other metals may also be present at elevated levels. Calcium usually enters the water from either $CaCO_3$, as limestone or chalk, or from mineral deposits of $CaSO_4$. Water hardness may be temporary or permanent.

Temporary hardness is hardness that can be removed by boiling or by the addition of lime (calcium hydroxide). It is caused by a combination of calcium ions and bicarbonate ions in the water. Boiling, which promotes the formation of carbonate from the bicarbonate, will precipitate calcium carbonate out of solution, leaving water that is less hard on cooling. Upon heating, less CO_2 is able to dissolve into the water. Since there is not enough CO_2, the reaction cannot proceed and therefore the $CaCO_3$ will not "dissolve" as readily. Instead, the reaction is forced to go from right to left (i.e., products to reactants) to reestablish equilibrium, and solid $CaCO_3$ is formed. Heating water will remove hardness as long as the solid $CaCO_3$ that precipitates out is removed. After cooling, if enough time passes, the water will pick up CO_2 from the air and the reaction will again proceed from left to right, allowing the $CaCO_3$ to "redissolve" in the water.

$$2Ca\left(HCO_3\right)_2 \xleftarrow{\text{boiling}} Ca_2CO_3 + CO_2 \uparrow + H_2O$$
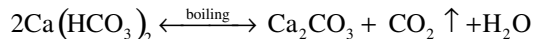
Permanent hardness is hardness that cannot be removed by boiling. It is usually caused by the presence of calcium and magnesium sulfates and/or chlorides in the water, which become more soluble as the temperature rises. Permanent hardness can be removed with ion exchange, or the lime-soda process.

In the ion exchange method, using *zeolite*, Ca and Mg ions are exchanged for Na.(see below for a detailed discussion of ion exchange treatment for water purification). In the lime-soda process, Ca and Mg ions are precipitated and removed by sedimentation and filtration. When water is softened with lime, it may be necessary sometimes to introduce CO_2, which reacts with any excess lime to form $CaCO_3$, which is precipitated before filtration.

9.3.11 Fluoridation

In some communities, small amounts of fluorides are added (about 1 ppm). It is believed that fluorides prevent dental decay. The fluorides used include sodium

fluoride, sodium silicofluoride, and ammonium silicofluoride.

Many North American and Australian municipalities fluoridate their water supplies in the belief that this practice will reduce tooth decay at a low cost, and about 70% of the water drunk in the US is fluoridated. Since fluoridation began in 1945, there has been a drop in dental decay, but fluoridation is still controversial in some communities.

9.3.12 Algae Control (and Control of Taste and Odors)

Objectionable tastes and odors in water may be taken as evidence of pollution or unwholesomeness even when this is not necessarily so. But the effect is that consumers lose confidence in the water.

Source of odors and tastes include:

1. *The growth of living microorganisms*: Some living things release taste-producing materials into water. For example, the Protozoa, *Synura* and *Uroglena* impart fishy taste to water and actinomycetes impart a "soil" taste to water. Many algae impart a taste of grass, and some of them produce other particularly objectionable odors, e.g., *Nitella*. Some of the compounds producing odors in water have been identified as geosmin and mucidione. The former is produced by the bluegreen alga, *Anabaena circinalis.* The observation that *Bacillus* spp. (esp. *B. cereus)* can degrade geosmin has led to the suggestion that the bacillus be used in water as a form of biological control of odors.
2. *The decomposition products of dead microorganisms plants and animals*: When bacteria (e.g., *Beggiatoa, Crenothrix*, and *Sphaerotilus),* plants, and animal die, their decaying parts produce odors in water.
3. *The production of methane and the reduction of sulfates to sulfides*
   These activities take place under anaerobic conditions and give rise to odors.
4. *Odor and taste-producing compounds in sewage and industrial effluents*
   Odor and taste-producing compounds are sometimes present in industrial and sewage effluents and these maybe carried into water; reaction compounds of chlorine with organic compounds also give rise to odors.

9.3.12.1 Methods for the Control of Algae and Taste and Odor

1. Algae may be destroyed in water by the addition of $CuSO_4$. In small amounts, $CuSO_4$ has not been shown to be toxic to man, but where fish are present in natural reservoirs, some fish may be affected.
2. Aeration also helps remove some odor.
3. The combined residual chlorine may have an objectionable taste if it is present in the form of chloro-organic compounds rather than as chloramines. The dose of chlorine should then be increased to destroy the compounds and leave Cl_2 as the free residual type.
4. Water may be passed over activated charcoal to remove odors and tastes.
5. Ozone may be used to destroy odor-producing compounds.

9.3.13 Color and Turbidity Removal

Color in water is derived from the microbial degradation of organic materials and from the extraction of organic materials from soil. It has been suggested that a humic-acid-like exudate from the aquatic fungus *Aurebasidium pullulans* may contribute to the yellow color found in water. Color-producing chemicals are complex chemically. Some are aromatic polyhydric methoxy carboxylic acids sometimes similar to tannic acids, which are of plant origin. Materials conferring color are negatively charged and usually occur along with chelated iron and manganese. Colored waters are usually surface waters. Color removal can be accomplished by metallic salts. For $Al(OH)_3$, the optimal pH is 5.5–7.0, while for ferric salts it is 3.5–4.5. The correct pH should be worked out in laboratory in "jar" tests.

Turbidity occurs mainly in surface waters and is absent in ground waters because soil particles filter off the colloidal materials, which cause turbidity. The colloidal particles are absorbed in the coagulants used in water purification.

9.3.14 Miscellaneous Treatments Water Purification

9.3.14.1 Plumbosolvency Removal

Plumbosolvency is the ability of a solvent, notably water, to dissolve lead. In older premises where lead pipes were used, plumbosolvent water can attack lead

pipes and any lead in solder used to join copper pipes, leading to increased lead levels in the tap water. On account of this, lead becomes a common contaminant of drinking water. Plumbosolvency of water can be countered by increasing the pH with lime or sodium hydroxide (lye), or by the addition of phosphate at the water treatment works.

9.3.14.2   Radium (Radioactivity) Removal

Underground waters associated with certain rock formations such as the crystalline granite rock of north-central Wisconsin exhibit low-level radioactivity, primarily from radium, although it could also come from uranium. Radioactivity levels are measured in "picocuries" per liter of water, (pCi/L). Health risks are low in consuming waters with low-level radioactivity. However, consuming it over a lifetime increases such risks. The consumption of radionucleotides in water poses increasing risks of cancers, and the US water standards permit zero amounts of alpha particles, beta particles, and photon emitters, Radium 226 and Radium 228, and uranium. In areas where the raw water is high in radioactivity, the water may be treated with synthetic zeolite ion exchange resins, which could remove about 90% of the radium. The water may also be purified with reverse osmosis.

9.3.14.3   Reverse Osmosis

Reverse osmosis is a filtration process that uses pressure to force a solution through a membrane; the solute is retained on one side and allowing the solvent passes at the other. It is so called because it is reverse of normal osmosis in which the solvent moves into where the solute concentration is, passing through a membrane.

9.3.14.4   Ion Exchange

Ion exchange resins are insoluble matrix or support structure normally in the form of small (1–2 mm diameter) beads, colored white or yellowish, made from an organic polymer material. The solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are preferred as they can be designed for specific applications. A matrix of pores on the surface of the beads, easily trap and release ions. The trapping of ions takes place only with simultaneous releasing of other ions, and hence the process is called ion exchange. Different types of ion exchange resin are fabricated to selectively prefer one or several different types of ions.

Ion exchange resins are widely used in different separation, purification, and decontamination processes. Most commonly, they are used for water softening and water purification. Before the introduction of resins, zeolites, which are natural or artificial alumino-silicate minerals and which can accommodate a wide variety of cations such as Na^+, K^+, Ca^{2+}, Mg^{2+}, were used.

For water softening, ion exchange resins are used to replace the magnesium and calcium ions, found in hard water, with sodium ions. When in contact with a solution containing magnesium and calcium ions, but a low concentration of sodium ions, the magnesium and calcium ions preferentially migrate out of solution to the active sites on the resin, being replaced in solution by sodium ions. This process reaches equilibrium with a much lower concentration of magnesium and calcium ions in solution than was started with.

The resin can be recharged by washing it with a solution containing a high concentration of sodium ions (e.g., it has large amounts of common salt (NaCl) dissolved in it). The calcium and magnesium ions migrate off the resin, being replaced by sodium ions from the solution until a new equilibrium is reached. This is the method of operation used in dishwashers that require the use of "dishwasher salt." The salt is used to recharge an ion exchange resin, which itself is used to soften the water so that limescale deposits are not left on the cooking and eating utensils being washed.

For water purification, ion exchange resins are used to remove undesirable constituents, e.g., copper and lead ions from solution, replacing them with more innocuous ions, such as sodium and potassium

Ion exchange is widely used in the food and beverage, metals finishing, chemical and petrochemical, pharmaceutical, sugar and sweeteners, ground and potable water, nuclear, softening and industrial water, semiconductor, power, and a host of other industries. It is particularly employed for removing radioactive compounds in water purifying processes.

9.3.14.5   Electrodeionization

Electrodeionization (EDI) is a water treatment process that removes ionizable species from liquids using electrically active media and an electrical potential to effect ion transport. It differs from other water purification technologies such as conventional ion exchange in that it is does not require the use of chemicals such as acid

and caustic soda. In traditional ion exchange units, after the contaminants are trapped onto the resin sites, the resin continues to exhaust and lose capacity. In EDI, the contaminants are continuously removed as they are attracted to one of the two electrical charges, and then migrate through the resin bed, through ion exchange membranes and into the concentrate stream where they are removed from the device.

Water splitting replaces the chemical regeneration process. For example, where R is impurity trapped on the mixed bed resin, the chemical regeneration process is

$$H_2SO_4 + R \rightarrow H^{2+} + RSO_4$$

$$NaOH + R \rightarrow OH^- + NaR$$
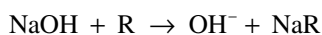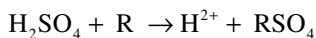
The hydrogen (H^+) ions and hydroxyl (OH^-) ions continuously regenerate the mixed resin in the EDI module. EDI is a polishing technology and requires reverse osmosis (RO) as pretreatment. The combination of RO–EDI provides the customer with a continuous, chemical-free system.

9.4 Purification of Bottled Water

Bottled water is very popular not only in the home, but it is also convenient for traveling, sports, and occasions where small quantities of drinking water with an assurance of good quality is expected. Many individuals do not however trust so-called purified water, in spite of what the manufacturers may write on the label. Many individuals believe that ordinary tap water is simply bottled. It would appear that in spite of this skepticism, some bottlers do make an effort to purify the water. Below is a flow chart of a system used by one bottler in the USA, which was made available to the author (Fig. 9.3).

9.5 Standards Required of Water

Water is used for many purposes, each of which requires that the water meets the standards, which in the main will ensure the health and safety of the users of the water. In this book, we have considered the use of water for drinking, recreation, and for the growth of shellfish. The standards required for each of these activities will be discussed in this section.

9.5.1 Standards Required for Drinking Water

Water is required by the human body constantly and an average adult probably consumes up to one liter or more per day. Since water must normally be consumed every day, unlike other food constituents, which may be eaten now and again, standards must be carefully set with the aim of protecting human health. Several considerations enter into the selection of standards for drinking water. These include:

(a) The public health statistics relating to morbidity and mortality due to a pathogen or chemical
(b) The population exposed
(c) The physical and chemical state of the substance
(d) The toxicity of the substance to man or to suitable experimental animals.
(e) The amount of the substance likely to be found in other sources

Water meant for human consumption must be free from chemical substances and microorganisms in types and amounts, which can be hazardous to health. Not only must it be safe but it must also be aesthetically acceptable. It is for this reason that the governments of various countries around the world set standards to be met in drinking water.

Ideally, the standards for drinking water should be uniform universally and used the world over. In practice, however, the standards depend on known and expected contaminants and the ability of the society or the government concerned to attain the standard; therefore, standards vary from country to country. The US standards will be discussed mainly, but standards of the European Union and the World Health Organization will also be mentioned for comparison.

In the United States, the US Environmental Protection Agency (EPA) sets the standards for drinking water. The Safe Drinking Water Act (SDWA), passed in 1974 and amended in 1986 and 1996, gives the EPA the authority to set drinking water standards. These standards are regulations that EPA sets to control the level of contaminants in the nation's drinking water. They are part of the Safe Drinking Water Act's "multiple barrier" approach to drinking water protection, which includes assessing and protecting drinking water sources; protecting wells and collection systems; making sure water is treated by qualified operators; ensuring the integrity of distribution systems; and making information available to the public on the quality of their drinking water. With
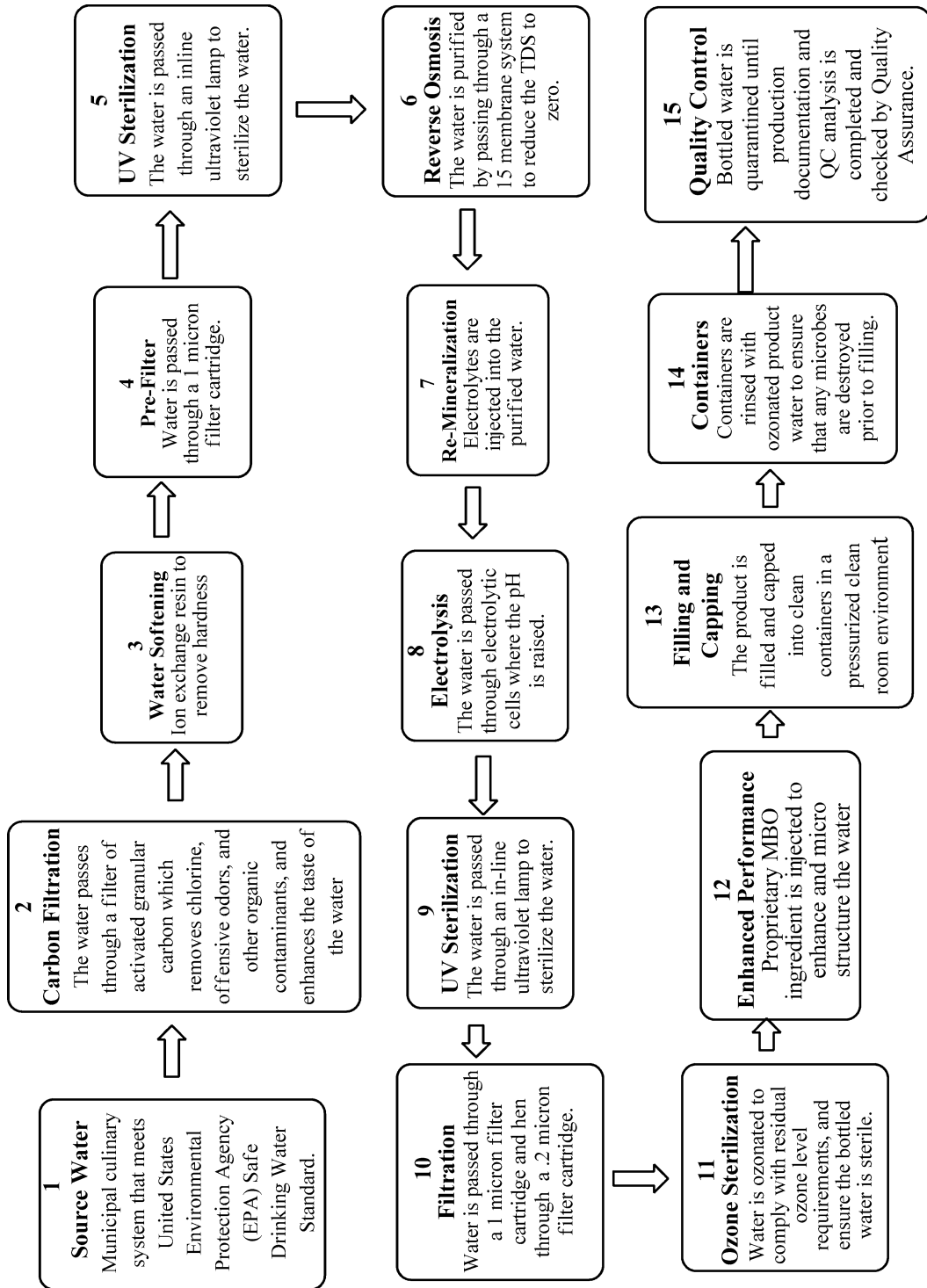
5
UV Sterilization
The water is passed through an inline ultraviolet lamp to sterilize the water.

4
Pre-Filter
Water is passed through a 1 micron filter cartridge.

3
Water Softening
Ion exchange resin to remove hardness

2
Carbon Filtration
The water passes through a filter of activated granular carbon which removes chlorine, offensive odors, and other organic contaminants, and enhances the taste of the water

1
Source Water
Municipal culinary system that meets United States Environmental Protection Agency (EPA) Safe Drinking Water Standard.

6
Reverse Osmosis
The water is purified by passing through a 15 membrane system to reduce the TDS to zero.

7
Re-Mineralization
Electrolytes are injected into the purified water.

8
Electrolysis
The water is passed through electrolytic cells where the pH is raised.

9
UV Sterilization
The water is passed through an in-line ultraviolet lamp to sterilize the water.

10
Filtration
Water is passed through a 1 micron filter cartridge and hen through a .2 micron filter cartridge.

11
Ozone Sterilization
Water is ozonated to comply with residual ozone level requirements, and ensure the bottled water is sterile.

12
Enhanced Performance
Proprietary MBO ingredient is injected to enhance and micro structure the water

13
Filling and Capping
The product is filled and capped into clean containers in a pressurized clean room environment

14
Containers
Containers are rinsed with ozonated product water to ensure that any microbes are destroyed prior to filling.

15
Quality Control
Bottled water is quarantined until production documentation and QC analysis is completed and checked by Quality Assurance.

Fig. 9.3 Flowchart for the manufacture of bottled water by a manufacturer

the involvement of EPA, States, Tribes, drinking water utilities, communities and citizens, these multiple barriers ensure that tap water in the United States and its territories is safe to drink. In most cases, EPA delegates responsibility for implementing drinking water standards to States and Tribes.

There are two aspects to the EPA water standards:

(a) The National Primary Drinking Water Regulation (NPDWR) or the primary standard
(b) The National Secondary Drinking Water Regulation (NSDWR) or the secondary standard

The primary standard is a legally enforceable standard that applies to public water systems. The primary standards protect drinking water quality by limiting the levels of specific contaminants that can adversely affect public health and are known, or anticipated, to occur in water. They take the form of maximum contaminant levels or treatment techniques. The secondary standards are a set of nonenforceable guidelines regarding contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply. However, States may choose to adopt them as enforceable standards.

Table 9.5 gives the maximum contaminant levels (MCLs) of the various contaminants expected in the environment of the USA. It is arranged in terms of microorganisms, disinfectants, disinfection by-products, inorganic chemicals, organic chemicals, and radionuclides. The standards are the highest in the world.

The World Health Organization (WHO) has produced standards (1993) for drinking water. These are however merely recommendations about minimal standards, which the WHO itself recognizes will not necessarily be attained in all countries of the world or regions due to differences in the economic and technological capabilities of various countries. The latest standards of the European Union (EU) (1998) are compared with those of the WHO (1993) in Table 9.6. It must be emphasized all standards are revised from time to time. For the most part, the EU standards are higher than the WHO standards. For example, bromate (Br) is not mentioned at all in the WHO standards, whereas a standard of 0.01 mg/l is set in the EU standards; for Manganese (Mn), the WHO standard is set at 0.5 mg/l whereas that of the EU is 0.05 mg/l. The WHO standards are to be found in an earlier document,

WHO (1984). The standards set by the USEPA (2009) are higher than those of the EU and the WHO. The US standards updated on March 19, 2009 are given in Table 9.4. EU and WHO standards are given side by side in Table 9.6.

9.5.1.1 The Microbiological Standards

All the standards state that no sample should contain fecal coliforms. In addition, the US standards specify the absence of *Cryptosporidium, Giardia lambia*, *and Legionella.* It is recommended that, to be acceptable, drinking water should be free from any viruses which affect man. This objective may be achieved *(a)* by the use of a water supply from a source which is free from wastewater and is protected from fecal contamination; or *(b)* by adequate treatment of a water source that is subject to fecal pollution.

Adequacy of treatment cannot be assessed in an absolute sense because neither the available monitoring techniques nor the epidemiological evaluation is sufficiently sensitive to ensure the absence of viruses. However, it is considered at present that contaminated source water may be regarded as adequately treated when the following conditions are met:

1. A turbidity of 1 NTU or less is achieved.
2. Disinfection of the water with at least 0.5 mg/l of free residual chlorine after a contact period of at least 30 min at a pH below 8.0.

The turbidity condition must be fulfilled prior to disinfection if adequate treatment is to be achieved.

Disinfection other than by chlorination may be applied provided the efficacy is at least equal to that of chlorination as described above. Ozone has been shown to be an effective viral disinfectant, preferably for clean water, if residuals of 0.2–0.4 mg/l are maintained for 4 min. Ozone has advantages over chlorine for treating water containing ammonia but, unfortunately, it is not possible to maintain an ozone residual in the distribution system

9.5.1.2 Turbidity

Turbidity is a measure of the cloudiness of water. It is used to indicate water quality and filtration effectiveness (e.g., whether disease-causing organisms are present). Higher turbidity levels are often associated with higher levels of disease-causing microorganisms such as viruses, parasites, and some bacteria. These organisms can cause symptoms such as nausea, cramps, diarrhea, and associated headaches. According to EPA

Table 9.5 USEPA's national primary and secondary standards for drinking water (As of 19 March, 2009) (http://www.epa.gov/safewater/contaminants/index.html) (Anonymous 2010b)

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Microorganisms				
Cryptosporidium	Zero	TT[c]	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste
Giardia lamblia	Zero	TT[c]	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste
Heterotrophic plate count	N/a	TT[c]	HPC has no health effects; it is an analytic method used to measure the variety of bacteria that are common in water. The lower the concentration of bacteria in drinking water, the better maintained the water system is.	HPC measures a range of bacteria that are naturally present in the environment
Legionella	Zero	TT[c]	Legionnaire's Disease, a type of pneumonia	Found naturally in water; multiplies in heating systems
Total coliforms (including fecal coliform and *E. Coli*)	Zero	5.0%[d]	Not a health threat in itself; it is used to indicate whether other potentially harmful bacteria may be present[e]	Coliforms are naturally present in the environment; as well as feces; fecal coliforms and *E. coli* only come from human and animal fecal waste.
Turbidity	N/a	TT[c]	Turbidity is a measure of the cloudiness of water. It is used to indicate water quality and filtration effectiveness (e.g., whether disease-causing organisms are present). Higher turbidity levels are often associated with higher levels of disease-causing microorganisms such as viruses, parasites, and some bacteria. These organisms can cause symptoms such as nausea, cramps, diarrhea, and associated headaches.	Soil runoff
Viruses (enteric)	Zero	TT[c]	Gastrointestinal illness (e.g., diarrhea, vomiting, cramps)	Human and animal fecal waste
Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Disinfection by-products				
Bromate	Zero	0.010	Increased risk of cancer	By-product of drinking water disinfection
Chlorite	0.8	1.0	Anemia; infants & young children: nervous system effects	By-product of drinking water disinfection
Haloacetic acids (HAA5)	N/a[f]	0.060[g]	Increased risk of cancer	By-product of drinking water disinfection
Total Trihalomethanes (TTHMs)	N/a[f]	0.080[g]	Liver, kidney, or central nervous system problems; increased risk of cancer	By-product of drinking water disinfection

Table 9.5 (continued)

Contaminant	MRDLG[a] (mg/L)[b]	MRDL[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Disinfectants				
Chloramines (as Cl_2)	MRDLG = 4[a]	MRDL = 4.0[a]	Eye/nose irritation; stomach discomfort, anemia	Water additive used to control microbes
Chlorine (as Cl_2)	MRDLG = 4[a]	MRDL = 4.0[a]	Eye/nose irritation; stomach discomfort	Water additive used to control microbes
Chlorine dioxide (as ClO_2)	MRDLG = 0.8[a]	MRDL = 0.8[a]	Anemia; infants & young children: nervous system effects	Water additive used to control microbes

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Inorganic chemicals				
Antimony	0.006	0.006	Increase in blood cholesterol; decrease in blood sugar	Discharge from petroleum refineries; fire retardants; ceramics; electronics; solder
Arsenic	0[g]	0.010 as of 01/23/06	Skin damage or problems with circulatory systems, and may have increased risk of getting cancer	Erosion of natural deposits; runoff from orchards, runoff from glass and electronics production wastes
Asbestos (fiber >10 μm)	7 million fibers per liter	7 MFL	Increased risk of developing benign intestinal polyps	Decay of asbestos cement in water mains; erosion of natural deposits
Barium	2	2	Increase in blood pressure	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits
Beryllium	0.004	0.004	Intestinal lesions	Discharge from metal refineries and coal-burning factories; discharge from electrical, aerospace, and defense industries
Cadmium	0.005	0.005	Kidney damage	Corrosion of galvanized pipes; erosion of natural deposits; discharge from metal refineries; runoff from waste batteries and paints
Chromium (total)	0.1	0.1	Allergic dermatitis	Discharge from steel and pulp mills; erosion of natural deposits
Copper	1.3	TT[h]; action level = 1.3	Short-term exposure: Gastrointestinal distress Long-term exposure: Liver or kidney damage People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	Corrosion of household plumbing systems; erosion of natural deposits
Cyanide (as free cyanide)	0.2	0.2	Nerve damage or thyroid problems	Discharge from steel/metal factories; discharge from plastic and fertilizer factories

Table 9.5 (continued)

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Fluoride	4.0	4.0	Bone disease (pain and tenderness of the bones); Children may get mottled teeth	Water additive, which promotes strong teeth; erosion of natural deposits; discharge from fertilizer and aluminum factories
Lead	Zero	TT[h]; action level = 0.015	Infants and children: Delays in physical or mental development; children could show slight deficits in attention span and learning abilitiesAdults: Kidney problems; high blood pressure	Corrosion of household plumbing systems; erosion of natural deposits
Mercury (inorganic)	0.002	0.002	Kidney damage	Erosion of natural deposits; discharge from refineries and factories; runoff from landfills and croplands
Nitrate (measured as nitrogen)	10	10	Infants below the age of 6 months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
Nitrite (measured as nitrogen)	1	1	Infants below the age of 6 months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome.	Runoff from fertilizer use; leaching from septic tanks, sewage; erosion of natural deposits
Selenium	0.05	0.05	Hair or fingernail loss; numbness in fingers or toes; circulatory problems	Discharge from petroleum refineries; erosion of natural deposits; discharge from mines
Thallium	0.0005	0.002	Hair loss; changes in blood; kidney, intestine, or liver problems	Leaching from ore-processing sites; discharge from electronics, glass, and drug factories

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Organic chemicals				
Acrylamide	Zero	TT[i]	Nervous system or blood problems; increased risk of cancer	Added to water during sewage/wastewater treatment
Alachlor	Zero	0.002	Eye, liver, kidney, or spleen problems; anemia; increased risk of cancer	Runoff from herbicide used on row crops
Atrazine	0.003	0.003	Cardiovascular system or reproductive problems	Runoff from herbicide used on row crops
Benzene	Zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer	Discharge from factories; leaching from gas storage tanks and landfills

(continued)

Table 9.5 (continued)

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Benzo(a)pyrene (PAHs)	Zero	0.0002	Reproductive difficulties; increased risk of cancer	Leaching from linings of water storage tanks and distribution lines
Carbofuran	0.04	0.04	Problems with blood, nervous system, or reproductive system	Leaching of soil fumigant used on rice and alfalfa
Carbontetrachloride	Zero	0.005	Liver problems; increased risk of cancer	Discharge from chemical plants and other industrial activities
Chlordane	Zero	0.002	Liver or nervous system problems; increased risk of cancer	Residue of banned termiticide
Chlorobenzene	0.1	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories
2,4-D	0.07	0.07	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops
Dalapon	0.2	0.2	Minor kidney changes	Runoff from herbicide used on rights of way
1,2-Dibromo-3-chloropropane (DBCP)	Zero	0.0002	Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton, pineapples, and orchards
o-Dichlorobenzene	0.6	0.6	Liver, kidney, or circulatory system problems	Discharge from industrial chemical factories
p-Dichlorobenzene	0.075	0.075	Anemia; liver, kidney, or spleen damage; changes in blood	Discharge from industrial chemical factories
1,2-Dichloroethane	Zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
1,1-Dichloroethylene	0.007	0.007	Liver problems	Discharge from industrial chemical factories
cis-1,2-Dichloroethylene	0.07	0.07	Liver problems	Discharge from industrial chemical factories
trans-1,2-Dichloroethylene	0.1	0.1	Liver problems	Discharge from industrial chemical factories
Dichloromethane	Zero	0.005	Liver problems; increased risk of cancer	Discharge from drug and chemical factories
1,2-Dichloropropane	Zero	0.005	Increased risk of cancer	Discharge from industrial chemical factories
Di(2-ethylhexyl) adipate	0.4	0.4	Weight loss, liver problems, or possible reproductive difficulties.	Discharge from chemical factories
Di(2-ethylhexyl) phthalate	Zero	0.006	Reproductive difficulties; liver problems; increased risk of cancer	Discharge from rubber and chemical factories
Dinoseb	0.007	0.007	Reproductive difficulties	Runoff from herbicide used on soybeans and vegetables
Dioxin (2,3,7,8-TCDD)	Zero	0.00000003	Reproductive difficulties; increased risk of cancer	Emissions from waste incineration and other combustion; discharge from chemical factories

Table 9.5 (continued)

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Diquat	0.02	0.02	Cataracts	Runoff from herbicide use
Endothall	0.1	0.1	Stomach and intestinal problems	Runoff from herbicide use
Endrin	0.002	0.002	Liver problems	Residue of banned insecticide
Epichlorohydrin	Zero	TT[1]	Increased cancer risk, and over a long period of time, stomach problems	Discharge from industrial chemical factories; an impurity of some water treatment chemicals
Ethylbenzene	0.7	0.7	Liver or kidneys problems	Discharge from petroleum refineries
Ethylene dibromide	Zero	0.00005	Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer	Discharge from petroleum refineries
Glyphosate	0.7	0.7	Kidney problems; reproductive difficulties	Runoff from herbicide use
Heptachlor	Zero	0.0004	Liver damage; increased risk of cancer	Residue of banned termiticide
Heptachlor epoxide	Zero	0.0002	Liver damage; increased risk of cancer	Breakdown of heptachlor
Hexachlorobenzene	Zero	0.001	Liver or kidney problems; reproductive difficulties; increased risk of cancer	Discharge from metal refineries and agricultural chemical factories
Hexachlorocyclo-pentadiene	0.05	0.05	Kidney or stomach problems	Discharge from chemical factories
Lindane	0.0002	0.0002	Liver or kidney problems	Runoff/leaching from insecticide used on cattle, lumber, gardens
Methoxychlor	0.04	0.04	Reproductive difficulties	Runoff/leaching from insecticide used on fruits, vegetables, alfalfa, livestock
Oxamyl (Vydate)	0.2	0.2	Slight nervous system effects	Runoff/leaching from insecticide used on apples, potatoes, and tomatoes
Polychlorinated-biphenyls (PCBs)	Zero	0.0005	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer	Runoff from landfills; discharge of waste chemicals
Pentachlorophenol	Zero	0.001	Liver or kidney problems; increased cancer risk	Discharge from wood preserving factories
Picloram	0.5	0.5	Liver problems	Herbicide runoff
Simazine	0.004	0.004	Problems with blood	Herbicide runoff
Styrene	0.1	0.1	Liver, kidney, or circulatory system problems	Discharge from rubber and plastic factories; leaching from landfills
Tetrachloroethylene	Zero	0.005	Liver problems; increased risk of cancer	Discharge from factories and dry cleaners

(continued)

Table 9.5 (continued)

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Toluene	1	1	Nervous system, kidney, or liver problems	Discharge from petroleum factories
Toxaphene	Zero	0.003	Kidney, liver, or thyroid problems; increased risk of cancer	Runoff/leaching from insecticide used on cotton and cattle
2,4,5-TP (Silvex)	0.05	0.05	Liver problems	Residue of banned herbicide
1,2,4-Trichlorobenzene	0.07	0.07	Changes in adrenal glands	Discharge from textile finishing factories
1,1,1-Trichloroethane	0.20	0.2	Liver, nervous system, or circulatory problems	Discharge from metal degreasing sites and other factories
1,1,2-Trichloroethane	0.003	0.005	Liver, kidney, or immune system problems	Discharge from industrial chemical factories
Trichloroethylene	Zero	0.005	Liver problems; increased risk of cancer	Discharge from metal degreasing sites and other factories
Vinyl chloride	Zero	0.002	Increased risk of cancer	Leaching from PVC pipes; discharge from plastic factories
Xylenes (total)	10	10	Nervous system damage	Discharge from petroleum factories; discharge from chemical factories

Contaminant	MCLG[a] (mg/L)[b]	MCL or TT[a] (mg/L)[b]	Potential health effects from ingestion of water	Sources of contaminant in drinking water
Radionuclides				
Alpha particles	None[g] ——— Zero	15 picocuries per Liter (pCi/L)	Increased risk of cancer	Erosion of natural deposits of certain minerals that are radioactive and may emit a form of radiation known as alpha radiation
Beta particles and photon emitters	None[g] ——— Zero	4 millirems per year	Increased risk of cancer	Decay of natural and man-made deposits of certain minerals that are radioactive and may emit forms of radiation known as photons and beta radiation
Radium 226 and Radium 228 (combined)	None[g] ——— Zero	5 pCi/L	Increased risk of cancer	Erosion of natural deposits
Uranium	Zero	30 ug/L as of 12/08/03	Increased risk of cancer, kidney toxicity	Erosion of natural deposits

Notes

[a]**Definitions**: Maximum Contaminant Level (MCL) – The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to MCLGs as feasible using the best available treatment technology and taking cost into consideration. MCLs are enforceable standards.

Maximum Contaminant Level Goal (MCLG) – The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.

Maximum Residual Disinfectant Level (MRDL) – The highest level of a disinfectant allowed in drinking water. There is convincing evidence that addition of a disinfectant is necessary for control of microbial contaminants.

Table 9.5 (continued)

Maximum Residual Disinfectant Level Goal (MRDLG) – The level of a drinking water disinfectant below which there is no known or expected risk to health. MRDLGs do not reflect the benefits of the use of disinfectants to control microbial contaminants.

Treatment Technique – A required process intended to reduce the level of a contaminant in drinking water.

[b]Units are in milligrams per liter (mg/L) unless otherwise noted. Milligrams per liter are equivalent to parts per million.

[c]EPA's surface water treatment rules require systems using surface water or ground water under the direct influence of surface water to (1) disinfect their water, and (2) filter their water or meet criteria for avoiding filtration so that the following contaminants are controlled at the following levels:

- Cryptosporidium: (as of 1/1/02 for systems serving >10,000 and 1/14/05 for systems serving <10,000) 99% removal.
- Giardia lamblia: 99.9% removal/inactivation
- Viruses: 99.99% removal/inactivation
- Legionella: No limit, but EPA believes that if *Giardia* and viruses are removed/inactivated, *Legionella* will also be controlled.
- Turbidity: At no time can turbidity (cloudiness of water) go above 5 nephelometric turbidity units (NTU); systems that filter must ensure that the turbidity go no higher than 1 NTU (0.5 NTU for conventional or direct filtration) in at least 95% of the daily samples in any month. As of January 1, 2002, turbidity may never exceed 1 NTU, and must not exceed 0.3 NTU in 95% of daily samples in any month.
- HPC: No more than 500 bacterial colonies per milliliter.
- Long-Term 1 Enhanced Surface Water Treatment (Effective Date: January 14, 2005); Surface water systems or (GWUDI) systems serving fewer than 10,000 people must comply with the applicable Long-Term 1 Enhanced Surface Water Treatment Rule provisions (e.g., turbidity standards, individual filter monitoring, Cryptosporidium removal requirements, updated watershed control requirements for unfiltered systems).
- Long-Term 2 Enhanced Surface Water Treatment Rule (Effective Date: January 4, 2006) – Surface water systems or GWUDI systems must comply with the additional treatment for Cryptosporidium specified in this rule based on their Cryptosporidium bin classification calculated after the completion of source water monitoring.
- Filter Backwash Recycling; The Filter Backwash Recycling Rule requires systems that recycle to return specific recycle flows through all processes of the system's existing conventional or direct filtration system or at an alternate location approved by the state.

[d]More than 0.5% samples are tested positive for coliform in a month. (For water systems that collect fewer than 40 routine samples per month, no more than one sample can be total coliform-positive per month.) Every sample that has total coliform must be analyzed for either fecal coliforms or E. coli if two consecutive TC-positive samples, and one is also positive for *E. coli* fecal coliforms, system has an acute MCL violation.

[e]Fecal coliform and E. coli are bacteria whose presence indicates that the water may be contaminated with human or animal wastes. Disease-causing microbes (pathogens) in these wastes can cause diarrhea, cramps, nausea, headaches, or other symptoms. These pathogens may pose a special health risk for infants, young children, and people with severely compromised immune systems.

[f]Although there is no collective MCLG for this contaminant group, there are individual MCLGs for some of the individual contaminants:

- Trihalomethanes: bromodichloromethane (zero); bromoform (zero); dibromochloromethane (0.06 mg/L): chloroform (0.07 mg/L).
- Haloacetic acids: dichloroacetic acid (zero); trichloroacetic acid (0.02 mg/L); monochloroacetic acid (0.07 mg/L). Bromoacetic acid and dibromoacetic acid are regulated with this group but have no MCLGs.

[g]The MCL values are the same in the Stage 2 DBPR as they were in the Stage 1 DBPR, but compliance with the MCL is based on different calculations. Under Stage 1, compliance is based on a running annual average (RAA). Under Stage 2, compliance is based on a locational running annual average (LRAA), where the annual average at each sampling location in the distribution system is used to determine compliance with the MCLs. The LRAA requirement will become effective April 1, 2012 for systems on schedule 1; October 1, 2012 for systems on schedule 2; and October 1, 2013 for all remaining systems.

[h]Lead and copper are regulated by a treatment technique that requires systems to control the corrosiveness of their water. If more than 10% of tap water samples exceed the action level, water systems must take additional steps. For copper, the action level is 1.3 mg/L, and for lead is 0.015 mg/L.

[i]Each water system must certify, in writing, to the state (using third-party or manufacturer's certification) that when acrylamide and epichlorohydrin are used in drinking water systems, the combination (or product) of dose and monomer level does not exceed the levels specified, as follows:

- Acrylamide=0.05% dosed at 1 mg/L (or equivalent)
- Epichlorohydrin=0.01% dosed at 20 mg/L (or equivalent)

National Secondary Drinking Water Regulations

National Secondary Drinking Water Regulations (NSDWRs or secondary standards) are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. EPA recommends secondary standards to water systems but does not require systems to comply. However, states may choose to adopt them as enforceable standards.

Table 9.5   (continued)

List of National Secondary Drinking Water Regulations

Contaminant	Secondary standard
Aluminum	0.05 to 0.2 mg/L
Chloride	250 mg/L
Color	15 (color units)
Copper	1.0 mg/L
Corrosivity	noncorrosive
Fluoride	2.0 mg/L
Foaming agents	0.5 mg/L
Iron	0.3 mg/L
Manganese	0.05 mg/L
Odor	3 threshold odor number
pH	6.5-8.5
Silver	0.10 mg/L
Sulfate	250 mg/L
Total dissolved solids	500 mg/L
Zinc	5 mg/L

Last updated on Wednesday, March 18th, 2009. http://www.epa.gov/safewater/contaminants/index.html

regulations, at no time can turbidity (cloudiness of water) go above 5 nephelometric turbidity units (NTU); systems that filter must ensure that the turbidity go no higher than 1 NTU (0.5 NTU for conventional or direct filtration) in at least 95% of the daily samples in any month. As of January 1, 2002, turbidity may never exceed 1 NTU, and must not exceed 0.3 NTU in 95% of daily samples in any month.

9.5.1.3 Chemical Standards

The EPA standards are by far the most comprehensive and include maximum quantities, expected in water, of disinfectants, by-products of disinfectants, inorganic chemicals such as antimony, arsenic, lead and mercury, organic chemicals such as acrylamide and benzene, radionucleotides such as alpha particles.

9.5.2 Standards Required for Recreational Waters

Standards set for drinking water include microbiological, chemical, radiological, turbidity, etc. For recreational waters, the standards appear to be mainly microbiological. Furthermore, since diseases, which can be contacted in recreational waters, are not enteric ones that enter by the oral–fecal route, it has been suggested that the standards should include the content of

water of other indicators, organisms besides those used for drinking water. Microorganisms that are used to assess the microbial quality of swimming pool and similar environments include heterotrophic plate count – HPC (a general measure of nonspecific microbial levels), fecal indicators (such as thermotolerant coliforms, *E. coli*), *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Legionella* spp. HPC, thermotolerant coliforms, and *E. coli* are indicators in the strict sense of the definition.

As health risks in pools and similar environments may be fecal or non-fecal in origin, both fecal indicators and non-fecally derived microorganisms (e.g., *P. aeruginosa*, *S. aureus*, and *Legionella* spp.) should therefore be examined. Fecal indicators are used to monitor for the possible presence of fecal contamination; HPC, *Pseudomonas aeruginosa*, and *Legionella* spp. can be used to examine growth, and *Staphylococcus aureus* can be used to determine non-fecal shedding. The absence of these organisms, however, does not guarantee safety, as some pathogens are more resistant to treatment than the indicators, and there is no perfect indicator organism.

In practice, enteric organisms have mainly been used. Thus, to protect human health from waterborne pathogens, the EPA recommends monitoring marine recreational waters for e*nterococci* (recommended threshold: geometric mean of 35/100 mL), and in

Table 9.6 Comparative assessment of EU and WHO water standards (From Lenntech Delft the Netherlands; http://www.lenntech.com/WHO-EU-water-standards.htm. With permission) (Anonymous 2009c)

	WHO standards	EU standards
Items	1993	1998
Suspended solids	No guideline	Not mentioned
COD	No guideline	Not mentioned
BOD	No guideline	Not mentioned
Oxidisability		5.0 mg/l O_2
Grease/oil	No guideline	Not mentioned
Turbidity	No guideline[a]	Not mentioned
pH	No guideline[b]	Not mentioned
Conductivity	250 μ/cm	250 μ/cm
Color	No guideline[c]	Not mentioned
Dissolved oxygen	No guideline[d]	Not mentioned
Hardness	No guideline[e]	Not mentioned
TDS	No guideline	Not mentioned
Cations (positive ions)		
Aluminum (Al)	0.2 mg/l	0.2 mg/l
Ammonia (NH4)	No guideline	0.50 mg/l
Antimony (Sb)	0.005 mg/l	0.005 mg/l
Arsenic (As)	0.01 mg/l	0.01 mg/l
Barium (Ba)	0.3 mg/l	Not mentioned
Beryllium (Be)	No guideline	Not mentioned
Boron (B)	0.3 mg/l	1.00 mg/l
Bromate (Br)	Not mentioned	0.01 mg/l
Cadmium (Cd)	0.003 mg/l	0.005 mg/l
Chromium (Cr)	0.05 mg/l	0.05 mg/l
Copper (Cu)	2 mg/l	2.0 mg/l
Iron (Fe)	No guideline[f]	0.2
Lead (Pb)	0.01 mg/l	0.01 mg/l
Manganese (Mn)	0.5 mg/l	0.05 mg/l
Mercury (Hg)	0.001 mg/l	0.001 mg/l
Molibdenum (Mo)	0.07 mg/l	Not mentioned
Nickel (Ni)	0.02 mg/l	0.02 mg/l
Nitrogen (total N)	50 mg/l	Not mentioned
Selenium (Se)	0.01 mg/l	0.01 mg/l
Silver (Ag)	No guideline	Not mentioned
Sodium (Na)	200 mg/l	200 mg/l
Tin (Sn) inorganic	No guideline	Not mentioned
Uranium (U)	1.4 mg/l	Not mentioned
Zinc (Zn)	3 mg/l	Not mentioned
Anions (negative ions)		
Chloride (Cl)	250 mg/l	250 mg/l
Cyanide (CN)	0.07 mg/l	0.05 mg/l
Fluoride (F)	1.5 mg/l	1.5 mg/l
Sulfate (SO4)	500 mg/l	250 mg/l
Nitrate (NO3)	(See Nitrogen)	50 mg/l
Nitrite (NO2)	(See Nitrogen)	0.50 mg/l

Microbiological parameters		
Escherichia coli	Not mentioned	0 in 250 ml
Enterococci	Not mentioned	0 in 250 ml
Pseudomonas aeruginosa	Not mentioned	0 in 250 ml
Clostridium perfringens	Not mentioned	0 in 100 ml
Coliform bacteria	Not mentioned	0 in 100 ml
Colony count 22°C	Not mentioned	100/ml
Colony count 37°C	Not mentioned	20/ml
Other parameters		
Acrylamide	Not mentioned	0.0001 mg/l
Benzene (C_6H_6)	Not mentioned	0.001 mg/l
Benzo(a)pyrene	Not mentioned	0.00001 mg/l
Chlorine dioxide (ClO_2)	0.4 mg/l	
1,2-Dichloroethane	Not mentioned	0.003 mg/l
Epichlorohydrin	Not mentioned	0.0001 mg/l
Pesticides	Not mentioned	0.0001 mg/l
Pesticides – total	Not mentioned	0.0005 mg/l
PAHs	Not mentioned	0.0001 mg/l
Tetrachloroethene	Not mentioned	0.01 mg/l
Trichloroethene	Not mentioned	0.01 mg/l
Trihalomethanes	Not mentioned	0.1 mg/l
Tritium (H_3)	Not mentioned	100 Bq/l
Vinyl chloride	Not mentioned	0.0005 mg/l

[a]Desirable: less than 5 NTU
[b]Desirable: 6.5–8.5
[c]Desirable: 15 mg/l Pt-Co
[d]Desirable: less than 75% of the saturation concentration
[e]Desirable: 150–500 mg/l
[f]Desirable: 0.3 mg/l

freshwater, *E. coli* (126/100 mL threshold) or *enterococci* (33/100 mL). EPA requires that at least five samples be taken at equally spaced interval over a 30-day period.

Drinking water regulations of the EPA specify the absence of *Legionella*, while the EU regulations specify the absence of *Pseudomonas*; these two organisms are more usually linked to recreational waters.

9.5.3 Standards Required for Shellfish Harvesting Waters

For shellfish harvesting, total coliform (not exceeding a geometric mean of 70 MPN per 100 mL, with not more than 10% of the samples taken during any 30-day

period exceeding 230 MPN per 100 mL) and fecal coliform monitoring (median concentration should not exceed 14 MPN per 100 mL, with not more than 10 % of the samples taken during any 30-day period exceeding 43 MPN per 100 mL) is recommended.

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