Swimming Pool Water Disinfection with Copper and Silver Ions

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Proper disinfection of swimming-pool water is essential to prevent the transmission of pathogenic microorganisms. Several viral, bacterial and parasitic agents have been associated to outbreaks in poorly disinfected recreational waters. Chlorine is the most commonly used disinfectant of swimming pools. This chemical has proved to be a very efficient disinfectant when used properly. However, its use may result in eye and skin irritation, undesirable odor and, more importantly, in the formation of trihalomethane compounds derived from the reaction of chlorine with organic matter. Alternative disinfectants include the use of electrolytically generated copper and silver ions. These metal ions are effective disinfectants against viruses and bacteria of concern in swimming pools. Furthermore, enhanced microbial inactivation is achieved when these metals are used in combination with low chlorine levels. Use of copper and silver ions in water systems currently used in swimming pools and spas may provide an alternative to high levels of chlorination.

Introduction

Chlorine has been used for many years in the disinfection of potable water because of its rapid inactivation of microorganisms. However, there are certain disadvantages with chlorination. The concentration of hypochlorite required to be effective in inactivating organisms like *Legionella* spp. in cooling tower water is relatively high and would most likely be corrosive to plumbing systems (Skaliy *et al.* 1990). Furthermore, levels of chlorine may be reduced from initially high levels to background levels rapidly (Fliermans *et al.* 1982), and may not provide a long–lasting residual effect, especially in systems operating at elevated temperatures. Sunlight and organic matter further deplete available chlorine. In addition, the formation of hazardous trihalomethane compounds, resulting from the reaction of chlorine with organic matter, is also a health concern.

Although hypochlorite can reduce numbers of *L. pneumophila* in cooling tower water to environmental levels through continuous and shock chlorination (Fliermans *et al.* 1982), isolates of *Legionella* spp. from regions of high chlorination have been shown to develop increased chlorine resistance (Kutcha *et al.* 1983).

To address these concerns, alternative disinfection treatments have been investigated. Copper and silver have been used for numerous years in the disinfection of water. Copper and silver are known to affect a number of microorganisms including bacteria, viruses, and algae (Landeen *et al.* 1989). They are believed to interfere with enzymes involved in cellular respiration (Domek *et al.* 1984), and to bind at specific sites to DNA (Rahn *et al.* 1973).

Inactivation by combined copper and silver has been shown to be relatively slow when compared to that of free chlorine. However, inactivation rates of bacterial indicator organisms (used to judge the sanitary quality of drinking and swimming pool water) with copper and silver in combination with chlorine were shown to be greater than those at comparable levels of free chlorine alone (Kutz *et al.* 1988; Landeen *et al.* 1989).

Microorganisms have a net negative charge at

Proceedings of the 1st Annual Chemistry Symposium
National Spa and Pool Institute – November 1996
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pH values near neutrality given by carboxyl, amino, guanidyl, and imidazole groups (Thurman and Gerba 1989). It has been suggested that cations such as copper and silver are electrostatically attracted to the negatively charged microorganisms and may then undergo reactions at the surface (Thurman and Gerba 1989). It is known that nonionized species cross the cell membrane better than ionized species. Once the former are inside the cell, ionization may occur due to a change of pH which allows metals ions to act at sites of RNA, DNA or enzymes. This mechanism of penetrating a charge barrier has been suggested as a means of explaining the greater disinfection efficiency of hypochlorous acid (HOCl) which possesses a neutral charge in contrast to the electronegatively charged hypochlorite ions (OCl^-) (Thurman and Gerba 1989). Copper has been used as an algicide for many years, and is reported to be one of the most toxic metals to heterotrophic bacteria in aquatic environments (Bitton and Friehofer 1978).

Metal ions may inactivate bacteria or viruses by reacting outside or inside the cell or virus either directly or indirectly. Inactivation targets may be proteins or nucleic acids. The possible mechanisms for inactivation by silver that have been proposed include: interference with electron transport, binding to nucleic acids, and interaction with cell membrane. The formation of insoluble compounds with anions, sulfhydryl groups, and many biological materials, such as enzymes, is responsible for the disinfecting activity of silver. Low concentrations of silver may enter a bacterial cell, possibly causing structural damage to the cell membrane. Upon entering the cell, the molecule may dissociate where the silver binds the DNA. The effect of silver nitrate on phage inactivation is very likely due to crosslinking of the DNA helix preventing transcription.

It has been suggested that proteins complexed with copper cannot function normally, thus cell death, or viral inactivation may follow. Copper may affect respiratory enzymes in the cell membrane of bacteria. For example, injured *E. coli* reduces the use of aerobic respiration and increases the use of fermentation pathways in the process of recovery (Domek *et al.* 1984). In addition, copper may also alter DNA. A single metal ion may link either two phosphates, two bases, or a phosphate and a base, preventing the DNA molecule from being transcribed. It has been shown that disinfection with copper and silver together results in a more efficient disinfection than when these metals are used alone (Landeen *et al.* 1989; Yahya, *et al.* 1992). A disinfectant that targets the nucleic acid of a microorganism may have a low efficiency when used alone. Likewise, a substance that targets the surface of a microorganism may also have a low efficiency. However, if used in combination, these substances may show an increased disinfection efficiency (Thurman and Gerba, 1989).

Legionella pneumophila is a ubiquitous aquatic organism which can survive under a wide range of environmental conditions. This organism is the causative agent of Legionnaires disease, a severe form of pneumonia in which aerosolization of contaminated water sources is believed to be the route of transmission. Since its isolation, following an outbreak of pneumonia at the 1976 American Legion Convention in Philadelphia, the annual number of reported cases of legionellosis in the United States has been increasing. *L. pneumophila* has been isolated from cooling towers and evaporative condensers, hot water tanks, and whirlpools. These water–recirculating systems often possess favorable growth conditions for *L. pneumophila*, such as elevated temperatures and mineral deposits, which can serve as a source of nutrients for biomasses and, in turn, support the growth of *Legionella* species. These devices are also known to produce aerosols and have implicated in numerous outbreaks. The concentration of hypochlorous acid required to be effective in inactivating *Legionella* species in cooling tower water are relatively high, and would most likely be corrosive to plumbing systems under actual conditions. Copper and silver are known to affect a number of microorganisms including bacteria, viruses, and algae. Inactivation by combined copper and silver has been shown to be relatively slow when compared with that of free chlorine; however, when these metals were added to low levels of free chlorine, inactivation rates of bacterial indicator organisms were shown to be greater than those at comparable levels of free chlorine alone.

Although silver has been used in Europe for swimming–pool disinfection, it has not been recommended in the US. A long contact time is required for effective activity therefore the process is undesirable for pool water disinfection. Furthermore, chlorides, ammonia, and organic matter interfere with silver disinfection. However, there has been some resurgence of interest in the use of silver ions, in conjunction with simultaneously generated copper ions, for reducing the amount of free chlorine required to achieve effective disinfection of swimming pool waters. In addition, one of the advantages of using copper and silver for water disinfection is that their disinfecting concentration is well below the U.S. E.P.A. maximum drinking water concentration (Table 1).

	Maximum in drinking water (mg/L)	Disinfecting concentration (µg/L)
Copper	1.3	200–700
Silver	0.9	20–70

Table 1 – U.S. E.P.A. maximum copper and silver levels in drinking water and disinfecting concentrations

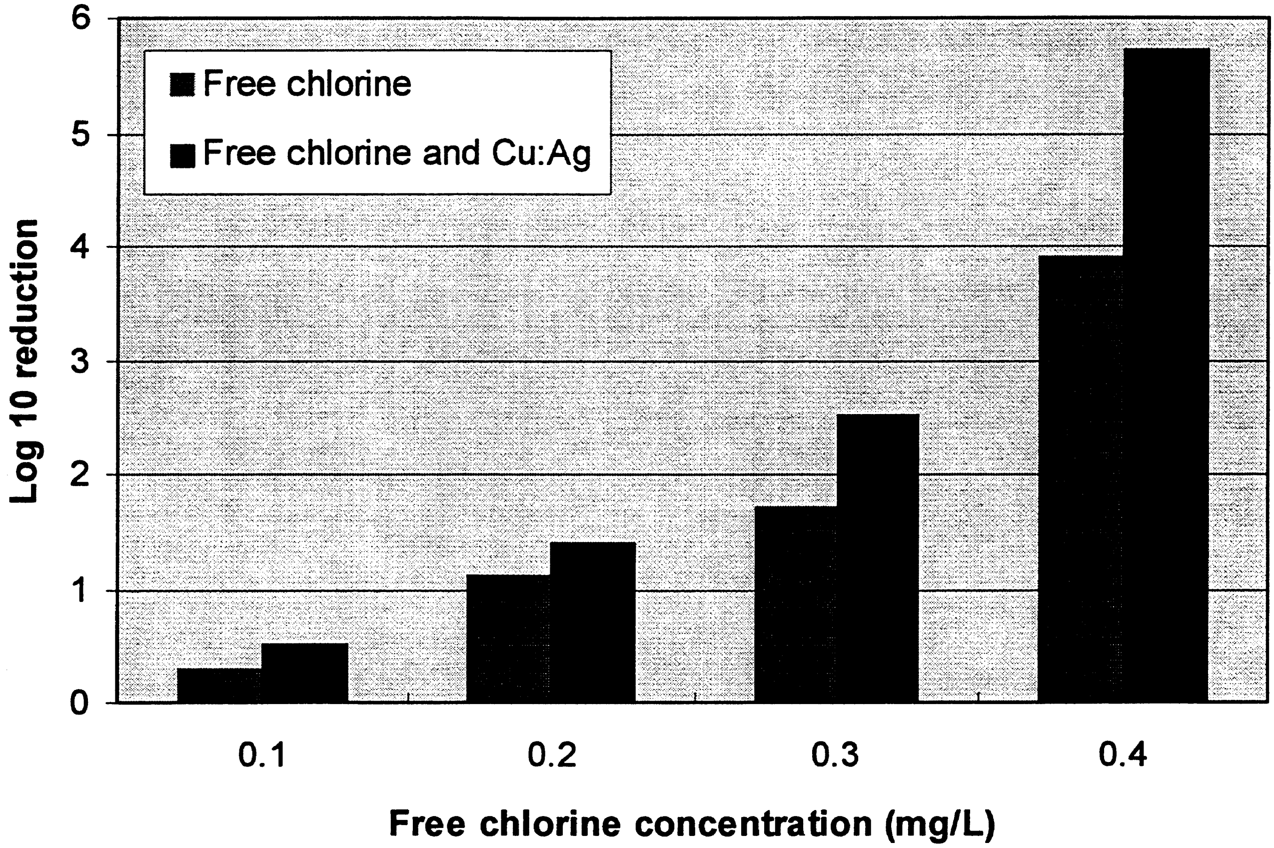

Figure 1 – Inactivation of *Legionella pneumophila* by exposure to generated copper:silver (400:40 µg/L) and various concentrations of free chlorine

Some disinfection studies (Landeen *et al.* 1989) using combined silver and copper have shown that the combination of these metals with chlorine results in an increased disinfection of *Legionella pneumophila* than that observed when the metals, or chlorine are used alone (Figure 1). These researchers also showed that disinfection with a combination of chlorine (0.2 mg/L) and copper:silver (400:40 µg/L) was more efficient at elevated temperatures (39–40°C) than at room temperature (21–23°C) (Figure 2). They suggested that the enhanced effects observed by the combined systems of free chlorine and copper:silver may be due to multiple sites of attack on the organism by both disinfectants. Free chlorine may alter the membrane permeability to facilitating the access of copper and silver to the interior of the cell.

Similar studies (Cassells 1990) using the protozoan *Naegleria fowleri* showed that a 3–$\log_{10}$ reduction was achieved within 10 minutes with 1 mg/L of free chlorine, while the same reduction was reached within 8 minutes when copper:silver (400:40 µg/L) was added (Figure 3). However, this author indicated that many factors can influence the disinfection of *Naegleria fowleri*. This organism may be protected from disinfectants by attaching to surfaces and particulate organic matter. Cassells (1990) indicated that disinfection of various organisms using copper:silver and/or chlorine varied markedly (Figure 4).

Summary

Copper and silver in combination with low chlorine concentrations offer an attractive alternative to disinfection with chlorine at higher concentrations. Unlike chlorine which dissipates from swimming pool waters, copper and silver do not dissipate, and adsorb to surfaces (Landeen 1989), and thus have been shown to provide a residual concentration for potential long term disinfection.

The results obtained in these studies should be extrapolated to normal swimming pool conditions cautiously, since they were conducted under controlled conditions. Further research needs to be carried out under different conditions such as hardness, turbidity, pH, and presence of organic matter among other environmental factors.

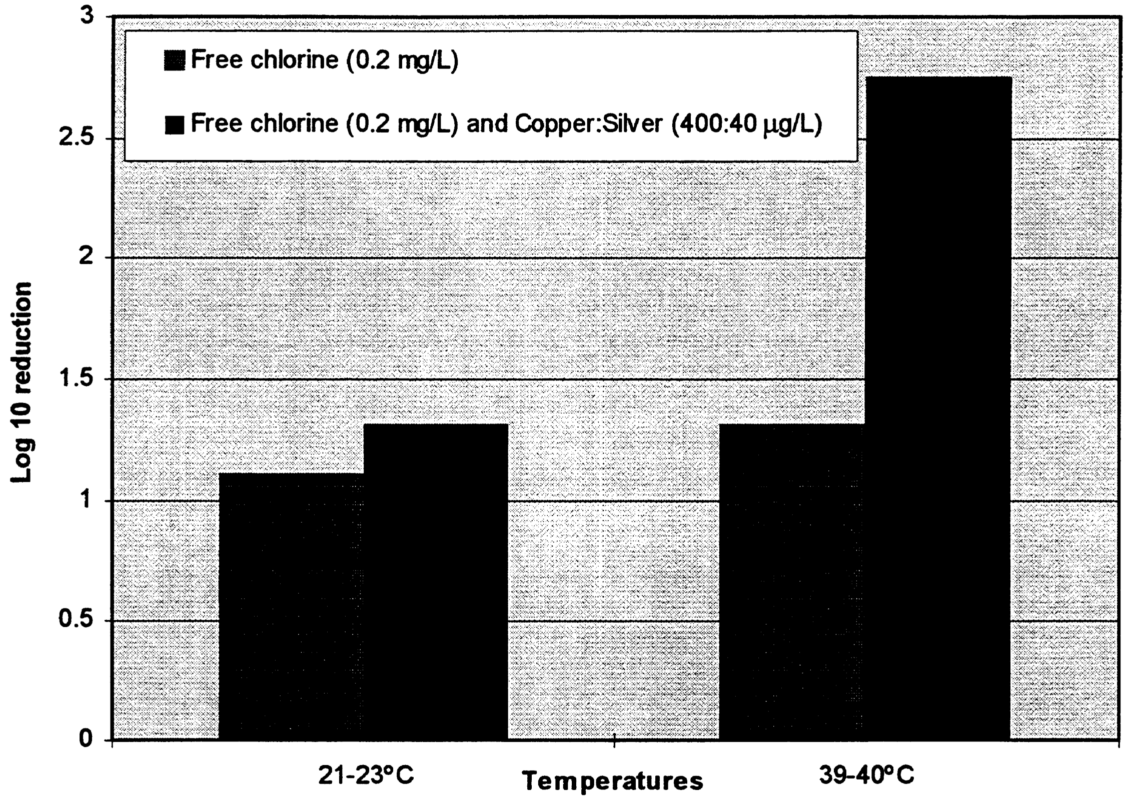

Figure 2 – Inactivation of *Legionella pneumophila* by exposure to generated copper:silver (400:40 µg/L) at two temperatures

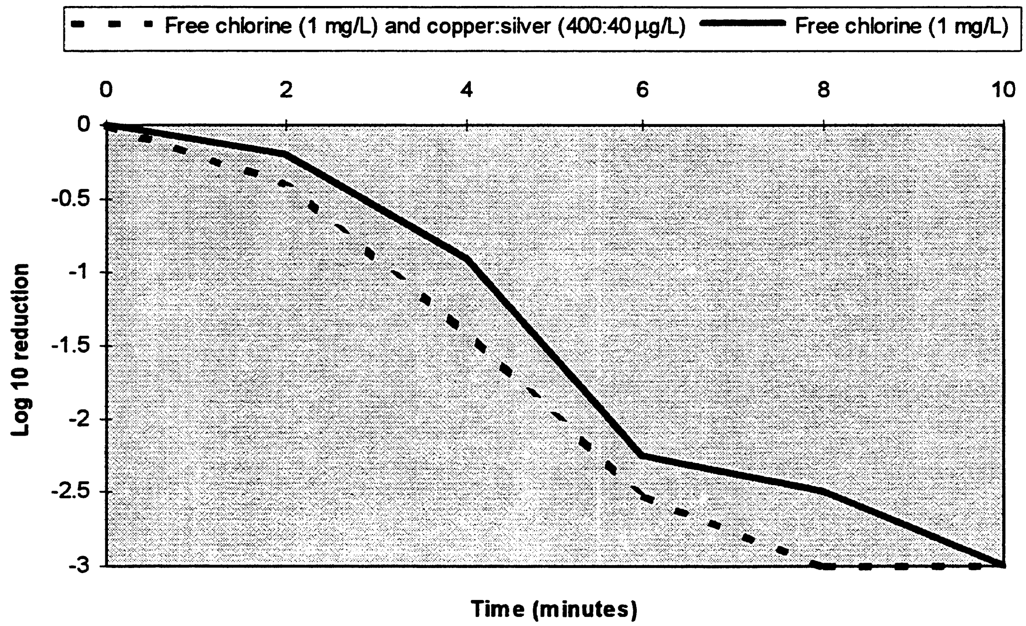

Figure 3 – Inactivation of *Naegleria fowleri* by exposure to generated copper:silver and/or chlorine

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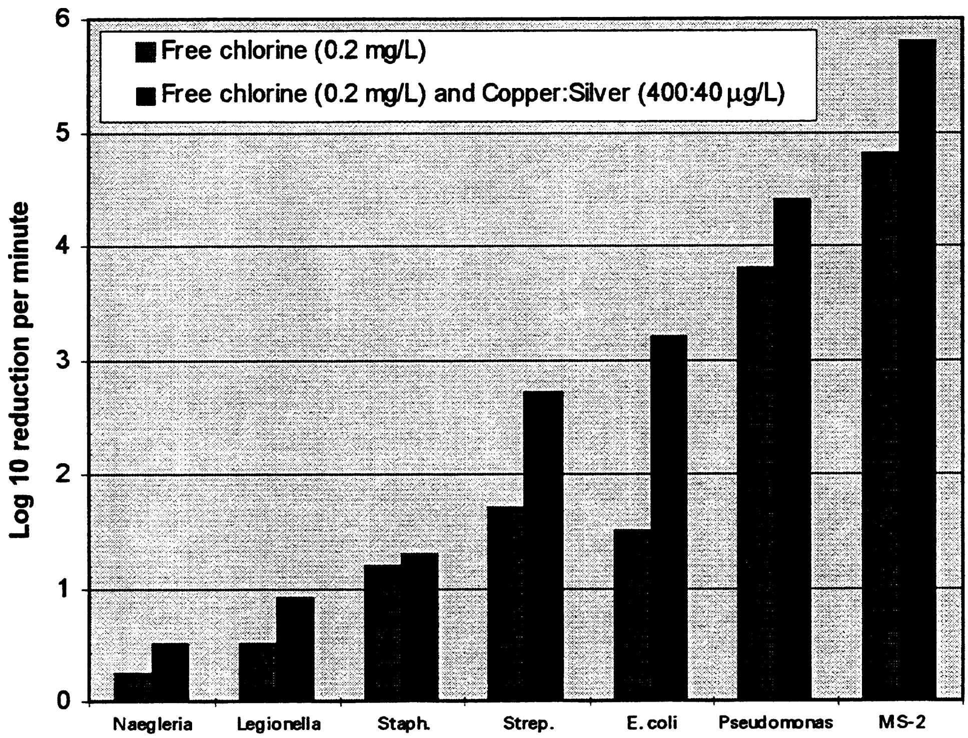

Figure 4 – Inactivation of various organisms exposed to chlorine and/or electrolytically generated copper:silver