# Progress in Pool Chemistry Research

# Understanding Disinfection Byproducts and Combined Chlorine

By Susan B. Rivera, Ph.D., CPO

Swimming pools require disinfection for inactivation of waterborne microbial pathogens. In most cases, a halogen-based compound—usually chlorine—is used as the disinfectant. Chlorine also serves the function of oxidizing contaminants introduced by the swimmers.

These disinfection (biological) and chemical (oxidative) reactions are some of the most complicated water chemistry systems to understand and manage. Recent research has provided insight into how UV and chlorine react with the bodily fluids and microorganisms introduced into pools, predominately by swimmers.

## Why chlorination?

Chlorine is the most cost-effective means of sanitizing a swimming pool. Recreational water outbreak analysis from the past 20 years demonstrates inadequately disinfected pools have been fully or partially responsible for the outbreaks since the chlorine-sensitive organisms simply were not inactivated in the waters.[1]

In the early 1900s, prior to adequate disinfection, tens of thousands of people died from waterborne disease. The filtration and disinfection of drinking water is widely acknowledged to be responsible for a large part of the 50 percent increase in life expectancy in this century. The US Centers for Disease Control (CDC) and Prevention recognizes the control of infectious diseases from cleaner water and improved sanitation as one of the top 10 public health achievements of the 20th century.

Unlike water distribution systems that deliver water to your tap, pool water is recirculated every six to eight hours through some type of filtration system. During this time, swimmers' activity provides a broad range of precursors with which disinfectants can react.

When chlorine reacts with these precursors, a variety of chemical reactions take place, including the formation of disinfection byproducts (DBPs). Standard pool filtration systems are ineffective at removing the precursors. In fact, it is the chlorine sanitizer that helps remove pollutants introduced by swimmers via oxidation reactions.

In the US, the accepted free available chlorine (FAC) concentration in pool water is one to five mg/L, but most operators maintain pools at two to four mg/L of FAC. FAC is defined as the sum of HOCl, $OCl^-$ and $Cl_{2(aq)}$ (all expressed as chlorine) and is commonly measured using a colorimetric method, known as the DPD method.

Several different pool test kits are available and utilize the DPD technology, either as a direct colorimetric measurement or a modification involving titration drop-wise to a colorless endpoint using ferrous ammonium sulfate (FAS). One of the concerns with chlorine is that the formation of chlorinated DBPs, especially volatile DBPs, may promote respiratory ailments.

The smell and irritant properties of swimming pool air have traditionally been attributed to inorganic chloramines, not free chlorine. Trichloramine has been reported to function as the irritant to the eyes and upper respiratory tract. However, studies have conflicted as to whether volatile chloramines are responsible for asthma and other respiratory illnesses linked to pools.

While researchers recognize the health benefits derived from swimming, others have identified exposure to the air above the pool water during swimming as a possible link to increased respiratory illnesses.

The reactions of chlorine with organic nitrogen-containing compounds (aka organic amines) in pool settings are still not well understood, but recent research is providing new insights into complicated pool chlorine chemistry. Historically, pool disinfection studies focused on the well-known reactions associated with the oxidation of ammonia, with trichloramine ($NCl_3$) being the most infamous volatile DBP. It was not until 2007 that studies of chlorine reactions with organic amines were reported. Two of these papers provide insight as to potential directions forward in pool management.

## Volatile disinfection byproduct analysis from model compounds known to be introduced by bathers

Air quality in indoor swimming pools has emerged as an area of concern with respect to human health. While researchers recognize the health benefits derived from swimming, others have identified exposure to the air above the pool water during swimming as a possible link to increased respiratory illnesses.

Dr. Ernest Blatchley and colleagues at Purdue University have recently made progress in developing a sensitive technique to measure DBPs. It is called membrane introduction mass spectrometry or MIMS. The technique may be used to detect and analyze volatile compounds in aqueous samples.

The membrane allows gases to enter into the mass spectrometer's chamber where molecules are identified according to their mass and then quantified by selected ion monitoring. MIMS can measure a variety of volatile molecules, providing quantitative and structural data about volatile DBPs in aqueous samples.

Using this technique, these researchers evaluated the volatile compounds released during reactions of chlorine with four model organic compounds known to be introduced by bathers.[2] The organic pollutants selected included urea, creatinine, L-histidine and L-arginine, all organic nitrogen-containing components found in human sweat and urine.

These results showed that common organic pollutants introduced during swimming activities contribute to the formation of trichloramine ($NCl_3$). Other DBPs, including chloroform ($CHCl_3$), cyanogen chloride (CNCl), dichloroacetonitrile ($CNCHCl_2$) and dichlormethylamine ($CH_3NCl_2$) were also detected, as shown in Table 1. This was the first time another precursor other than ammonia had been demonstrated to produce $NCl_3$.

**Table 1.**

| Model compound | Volatile chloramine produced |
|---|---|
| Urea | $NCl_3$ – most abundant source of trichloramine |
| Creatinine | $NCl_3$, $CH_3NCl_2$ |
| L-histidine | $NCl_3$, $CNCHCl_2$, CNCl |
| L-arginine | $NCl_3$ |

### *Volatile disinfection byproduct analysis of chlorinated indoor swimming pools*

The researchers went on to look at the distribution of disinfection byproducts in 11 different types of indoor pools over a six-month period.[3] One of these was a spa.

The goal of the study was to identify volatile DBPs and their concentration ranges in chlorinated indoor swimming pools. Ten volatile inorganic and organic chloramines were identified as persistently existing, though the concentrations varied by nearly four orders of magnitude between the pools analyzed.

In addition to the volatile DBPs identified in the model study described above, brominated DBPs were also identified. It is thought that these compounds were derived from bromide that tends to accumulate over time unless water is exchanged.

Bromide is oxidized by chlorine to produce HOBr, the cousin to HOCl. HOBr can lead to the formation of brominated DBPs. Among halogenated DBPs, bromine-substituted compounds tend to display greater toxicity than their chlorinated analogs.

Free chlorine was also measured using DPD technology. This is the technology used in many pool test kits. The research indicated that 16.7 percent of the samples had a free chlorine concentration below 1.0 mg/L, the suggested lower limit by the National Swimming Pool Foundation (NSPF).

Several of the pool water samples had undetectable amounts of FAC, a cause for great concern. Pool operations rely on the presence of free chlorine to inactivate waterborne microbial pathogens and oxidize pollutants, even if other technologies such as UV are in place.

Combined chlorine (CC) was also measured using both DPD technology and MIMS, the more accurate analytical method. In the case of MIMS, direct quantitative measurements can be made while with DPD, CC is calculated from the total chlorine (TC) and FAC measurements using the following equation:

CC = TC- FAC

### *Comparison*

The methods showed that the DPD method consistently overestimates inorganic chloramine content in swimming pools. Using the MIMS method, 75.9 percent of the pools had inorganic combined chlorine concentrations that exceed the NSPF guideline of 0.2 mg/L for pools and 0.5 mg/L for spas.

Among the spa samples, 29.0 percent were above 0.5 mg/L. Using DPD, the number of pools over the 0.5 mg/L CC limit were 95.9 percent of pool samples and 96.8 percent of spa samples. The sources of interference of the DPD reactions are largely undefined, but their existence suggests that use of DPD-based methods as the only method to estimate inorganic chloramines may lead to inappropriate pool maintenance practices, particularly related

## Seven Tips For Safer Home Swimming Pools and Hot Tubs

Each year, stories about home pool or hot tub tragedies make headlines across the county. With millions enjoying their backyard pools and hot tubs, the need for home pool and hot tub safety is urgent.

The American Red Cross and National Swimming Pool Foundation® want all home pool and hot tub owners to make safety their priority. Learn more about pool and spa safety from the Red Cross and NSPF by visiting their websites at www.redcross.org and www.nspf.org.

They encourage all pool and spa owners to follow these safety guidelines:

**1.** Secure your pool with appropriate barriers. Completely surround your pool with a four-foot-high fence or barrier, with a self-closing, self-latching gate. Install alarms on any doors leading to the pool that sound when opened unexpectedly. Place a safety cover on the pool or hot tub when not in use and remove any ladders or steps used for access. Consider installing a pool alarm that goes off if anyone enters the pool.

**2.** Keep children under active supervision at all times. Stay in arm's reach of young children. Designate a responsible person to watch the water when people are in the pool—never allow anyone to swim alone. Have young or inexperienced swimmers wear a US Coast Guard-approved life jacket.

**3.** Ensure everyone in the home knows how to swim well by enrolling them in age-appropriate water orientation and learn-to-swim courses.

**4.** Keep your pool or hot tub water clean and clear. Use proper chemical levels, circulation and filtration. Regularly test and adjust chemical levels to minimize the risk of earaches, rashes or more serious diseases.

**5.** Establish and enforce rules and safe behaviors, such as 'no diving,' 'stay away from drain covers,' 'swim with a buddy' and 'walk please.'

**6.** Ensure everyone in the home knows how to respond to aquatic emergencies by having appropriate safety equipment and taking water safety, first aid and CPR courses from the Red Cross.

**7.** Enroll in the two-hour Home Pool Essentials online course (www.HomePoolEssentials.org) for only $19.95. This class describes steps you can take to help prevent tragedy and how to care for your pool and hot tub. It includes a 30-page resource guide and six months access to the site.

to the amounts of chlorine needed to 'shock' a pool. Shock chlorination was largely developed based on knowledge of the so-called breakpoint reaction where ammonia is oxidized to nitrogen gas, with mono-, di- and tri-chloramine as intermediates along the pathway.

## Outcome goals

If the DPD reaction is also measuring organic chloramines, then the philosophy surrounding chlorine shocking may need to be adjusted. Possibilities include installing automated controllers to periodically increase chlorine concentrations overnight to help drive the breakpoint of the inorganic chloramines in the pool, allowing the FAC to return to acceptable levels prior to opening the next morning.

This type of strategy would avoid the need to dechlorinate. Another strategy is to install additional technologies to supplement the disinfection and oxidation properties of chlorine. These include UV, which has shown promise in photolysing inorganic chloramines in pools with good filtration.[4]

Another goal for industry leaders should be to actively promote the development and manufacture of a low-cost device to accurately measure volatile inorganic and organic compounds. Specific goals for the industry might include:

1) Developing an affordable field-ready MIMS device

2) Guidance documents to assist pool operators and regulators to determine when a pool is truly out of compliance for combined chlorine

3) Additional third-party studies to evaluate DBPs associated with ozone, chlorine dioxide, monopersulfate, electrochemical methods of generating chlorine-based disinfectants and other commonly used disinfection and oxidation chemicals. These data can then be used to better understand the mechanism of formation for DBPs and the subsequent advantages and disadvantages of each type of disinfection chemistry. Not all oxidants and chlorine-based disinfectants are equal.[5]

Great progress in understanding pool chemistry has emerged over the past few years. As technologies and analytical approaches improve, consideration of how to alter pool management guidelines and policies will follow. The information provided by the research will be beneficial in the development of multibarrier treatment technologies and control strategies to provide adequate disinfection in the pool while minimizing DBP formation.

Increased efforts have also been made to educate the public regarding the benefits of showering before entering the water and refraining from urinating in the pool. Minimizing precursor introduction (lotions, dried sweat, dirt, urine) will likely go a long way to improving swimming pool chemistry.

## References

1. Centers for Disease Control Healthy Swimming Website http://www.cdc.gov/healthySwimming/

2. J. Li and E. R. Blatchley, "Volatile Disinfection Byproduct Formation Resulting from Chlorination of Organic-Nitrogen Precursors in Swimming Pools," Environmental Science & Technology. 2007, 41, 6732-6739.

3. W.A. Weaver, J. Li, Y. Wen, J. Johnston, M.R. Blatchley and E. R. Blatchley, "Volatile Disinfection By-product Analysis from Chlorinated Indoor Swimming Pools," Water Research 2009, 43, 3308-3318.

4. J. Li and R.R. Blatchley, "UV Photodegradation of Inorganic Chloramines," Environmental Science & Technology. 2009, 43, 60-65.

5. One of these technologies includes mixed oxidants and two include in-line salt water chlorinators and mixed oxidants. A summary of disinfection and oxidation advantages of mixed oxidants can be found in the document entitled "Master Features Summary.pdf" located in MIOX's library at www.miox.com.

## About the author

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## About MIOX Corporation

*MIOX Corporation, based in Albuquerque, NM, is focused on solving one of the world's most pressing issues: the need for affordable, safe and healthy water. MIOX's patented water disinfection technology replaces the need to purchase, transport and store dangerous chemicals. The company has over 1,500 installations, with equipment used in over 30 countries. MIOX equipment is used in recreational water venues, in hundreds of communities across the US for public drinking water systems, water reuse projects and a variety of commercial and industrial applications. More information is available at www.miox.com.*