Irritant Effect (Conjunctivitis) of Chlorine and Chloramines in Swimming Pool Water

Vom Wasser, Vol. 45, pp. 17-28 (1975)

Dr. *D. Eichelsdörfer* and *J. Slovak* [Dipl.-Chem., chemistry degree], Institute of Water Chemistry and Chemical Balneology of the Technical University of Munich; *K. Dirnagl* [Dipl.-Phys., degree in physics] and *K. Schmid* [cand. med., Candidate for medical degree], Institute of Medical Balneology and Climatology of the University of Munich

Abstract

The mucous membrane irritation and unpleasant odors often observed in chlorinated pool water on the one hand is attributed to a chlorine concentration that is too high; on the other hand, it is also suspected that the blame for these unacceptable side effects of chlorination does not fall on chlorine itself but rather on chlorine-nitrogen compounds that are formed by reactions between chlorine and nitrogen-containing pollutants in the pool water. Since this question, which so far has not been experimentally examined, is of considerable interest for treatment, testing, and assessment of swimming pool water, the effect of certain aqueous chlorine and chloramine solutions on rabbit conjunctiva was studied. For the first time, experimental evidence has been obtained that chlorine combined with nitrogen [compounds] is considerably more irritating than free active chlorine.

The most important task of pool water treatment is to achieve a water quality in all parts of the swimming pool facility that eliminates any risk of infection for the bathers. In addition to these basic epidemiological requirements, the pool water should also be acceptable from a general hygienic standpoint; i.e., in the broadest sense, it should be free of constituents and properties that could have a negative effect on the health and also the well-being of the bathers.

In order to meet the most important requirement for swimming pool water (elimination of any risk of infection for the bathers), a disinfectant must be routinely added to the pool water that has a sufficiently fast microbial kill rate or can inactivate viruses even with a short contact time, and that maintains its bactericidal and viricidal properties during its entire residence time in the swimming pool.

The problem

Mainly chlorine and chlorine compounds have been used in pool water treatment since about 1920 [1]. They have been quite reliable for over 50 years now for disinfection of swimming pool water, and to date practically no other disinfectants have been able to replace them on a significant scale. Thus even according to the "Guidelines for treatment of swimming pool water" published in 1972 [2], at the moment only the following disinfection methods are accepted and approved:

Chlorine bleach solution method (hypochlorite method)
Hypochlorous acid method
Chlorine/chlorine dioxide method

Hypochlorite method with chlorine generation from sodium chloride by electrolysis.

But the chlorine-based methods, when improperly applied, often lead to irritation of the conjunctiva ("conjunctivitis") and to problems with the nasopharyngeal mucosa. In addition, characteristic and unpleasant odors often occur that are known by the term "indoor pool smell". So because of these undesirable properties, many attempts have been made to replace chlorine by other disinfectants. However, in addition to their well-known and excellent disinfectant effect, chlorine and some chlorine compounds also have considerable reactivity and oxidizing capacity, which is an important factor in the treatment process for oxidative degradation of organic pollutants in pool water that cannot easily be sacrificed. For this reason alone, a number of other disinfectants for pool water treatment that come under discussion again and again are generally not suitable, or else are suitable only for special combinations of methods.

Chlorine dissolved in water reacts as in (1) and (2) to form hypochlorous acid and hydrochloric acid or hypochlorite and chloride ions.

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \qquad (1)$$
$$HOCl \leftrightarrow H^+ + OCl^- \qquad (2)$$

At the usual pH values in swimming pool water (between 7 and 8) and chlorine concentrations from just a few tenths of a milligram to a few milligrams per liter, the equilibrium for the reaction in Eq. (1) is shifted to a large extent toward the right; so the concentration of unhydrolyzed chlorine in pool water is extremely low and is on the order of magnitude of about 10^{-10} mol/L Cl_2, practically only in trace amount range.

Dissolved elemental chlorine, hypochlorous acid, and hypochlorite ions, the concentration ratios of which depend in particular on the pH, are collectively called "free active chlorine", and the germicidal effect is primarily attributed to them. In swimming pool water, however, depending on the concentration ratios, the "free chlorine" reacts partially or completely with inorganic and organic pollutants introduced into the water from the bathers, either by washing out from the body or by secretion and excretion. In particular, nitrogen-containing pollutants such as urea, creatinine, and ammonia can form chlorine-nitrogen compounds in which the chlorine to a certain extent still has oxidizing and disinfectant properties. These compounds are jointly called by the collective term "combined active chlorine".

On the one hand, too high a chlorine concentration is considered as responsible for the frequently occurring irritant effects and unpleasant odors in chlorinated pool water, but information in the literature is very contradictory. While some authors have observed eye irritation symptoms in swimmers even at 0.7 mg/L free chlorine, others report that even at concentrations above 2 mg/L chlorine they do not detect any eye changes caused by irritation. *Mood* [3], who studied the effect of free chlorine on the conjunctiva with the help of the Yale University swim team, limited the study to only two different chlorine concentrations (0.05 and 0.5 mg/L Cl_2) at pH 7 and at pH 8. A number of subjective symptoms and objective signs of eye changes were evaluated. With an elevated chlorine content, in particular at pH 7, the subjectively perceived symptoms of the swimmers were clearly increased, but no correlation could be established between the reddening of the conjunctiva and the chlorine content or the pH value. In the studies, the combined chlorine content was in the range of a few hundredths of a milligram per liter and was not considered.

For quite some time it also has been suspected that the chlorine-containing nitrogen compounds called "combined chlorine" in particular are the real reason for the irritation symptoms and the characteristic indoor pool smell for chlorinated swimming pool water. But this suspicion is obviously based only on isolated observations. We cite as an example *Voss* [4], who reported that for freshly filled swimming pool water, no unpleasant odors or irritation symptoms appeared even at 5 mg/L free chlorine, while after just three days of operation with regular increase in combined chlorine, both the chlorine smell and eye irritation were observed. Indeed, a large number of similar indications are found in the literature; however, no systematic study of the different degrees of irritation from chlorine and various chlorine-nitrogen compounds in pool water has been reported so far.

Once *Allgayer* and *Korzinek* [5] at the Institute of Medical Balneology and Climatology of the University of Munich recently successfully developed a method for studying the irritant effect of different medicinal products and reagent solutions on rabbit conjunctiva, we had the experimental prerequisites for examining the question of a possible difference in degree of irritation between free and combined chlorine in animal experiments.

Nitrogen-containing pollutants in pool water

Formation of combined chlorine in swimming pool water is causally related to nitrogen-containing pollutants that can be released into the water from the bathers by elution from their skin or by exudation of sweat or excretion of urine. According to *Hässelbarth* [6], the total amount of combined nitrogen released into the water per bather is from 0.8 g to 1 g. A clue to the kind of nitrogen compounds that can be eluted from skin comes from a compilation by *Kuno* [7] of the average nitrogen content of sweat and its distribution among the predominant nitrogen compounds.

According to the latter, sweat contains about 1 g/L nitrogen, mainly in the form of urea, ammonia, amino acids, and creatinine. But we should point out here that the composition of sweat or skin eluates fluctuates over an extremely broad range, depending on conditions; the values given in Table 1 are averages. Considerable amounts of nitrogen compounds can get into pool water through excretion of urine in particular. The distribution of total nitrogen among the predominant nitrogen compounds (Table 2) was calculated from statistical averages of 24-hour urine samples [8].

Table 1. Predominant nitrogen compounds in sweat as a percentage of total nitrogen.

Nitrogen compound	Nitrogen content in sweat, in mg/L	Fraction of total N, in %
Urea N	682	69.0
Ammonia N	176	17.8
Amino acid N	45	4.6
Creatinine N	7	0.7
Nitrogen in other compounds	79	7.9
Total N	989	100.0

Table 2. Predominant nitrogen compounds in urine as a percentage of total nitrogen.

Nitrogen compound	Nitrogen content in urea, in mg/L	Fraction of total N, in %
Urea N	10 237	83.8
Creatinine N	636	5.2
Ammonia N	559	4.6
Amino acid N	279	2.3
Nitrogen in other compounds	499	4.1
Total N	12 210	100.0

Although over 80% of total nitrogen in urine is present in the form of urea and in contrast the ammonia content is comparatively small (about 5%), often significant ammonia concentrations are found in pool water, which obviously is only formed secondarily from urea, e.g., by enzyme catalyzed hydrolysis.

The question of which chlorine-nitrogen compounds specifically form in swimming pool water can be answered neither simply nor in general, since the reactions between chlorine and the nitrogen-containing pollutants are both affected by the pH and depend to a considerable extent on the concentration ratios of the reactants. In addition, chlorine-nitrogen compounds in general are substances capable of further reactions and are stable only over a particular range. For example, according to *Palin* [9], monochloramine in excess ammonia is stable in the pH range between 6 and 10, while dichloramine exists only in the acid pH range between 3.5 and 7; for pH values of about 7, dichloramine is formed only in trace amounts. But some authors have described the appearance of dichloramine in the neutral to slightly alkaline range for swimming pool water. However, the analysis methods employed, using *o*-toluidine [[1]] or N,N-diethyl-*p*-phenylenediamine (DPD), are not substance-specific. Thus *Lomas* [10] was able to prove that, for example, monochlorocreatinine can produce a false positive for dichloramine in such tests. The situation is similar for urea, which can form more or less stable chlorourea compounds,

[1] Translator's Note: Corrected misprint in German: "Tolidin" should be "Toluidin" (toluidine).

depending on the concentration ratios and the pH. Not much is yet known specifically about reactions of creatinine as well as various amino acids with chlorine, or about the stability of their chloro-substituted products in swimming pool water.

Preparation of test solutions

In order to create clear-cut conditions for our tests, instead of swimming pool water we used test solutions with definite amounts of "free chlorine", monochloramine (as a potential major component of "combined chlorine" in pool water) and monochlorourea, since urea is certainly one of the major pollutants in pool water. Munich tap water was used as the blank and to prepare the test solutions; this water has moderate hardness of 17° (degrees German) and is practically completely free of organic matter.

Test solutions with different contents of free active chlorine were prepared by appropriate dilution of a chlorine water stock solution (neutralized with NaOH) with nutrient-depleted Munich tap water.

The monochloramine solutions were prepared by slowly adding dilute chlorine water to an ammonium chloride solution, in the mole ratio chlorine:nitrogen = 1:1.25. The pH of the solutions was adjusted to the pH of Munich tap water (about 7.5). By fractional separation of the individual forms of combined chlorine according to the N,N-diethyl-*p*-phenylenediamine method (DPD method) of *Palin* [11] and by determination of the sum of the total chlorine content, we were able to establish that the test solutions contained practically only monochloramine and no free chlorine. In addition, we studied test solutions with higher concentrations (about $5 \cdot 10^{-4}$ molar concentration) spectroscopically. Since the UV spectra of monochloramine (λ_{max} 243 nm) and dichloramine (λ_{max} 297 nm) are sufficiently different [12, 13], it could be definitely established that the solutions contained exclusively monochloramine; dichloramine could not be detected spectroscopically.

For the monochlorourea test solutions, first concentrated monochlorourea stock solutions had to be prepared, since the reaction between urea and chlorine in dilute aqueous solutions proceeds very slowly and not quantitatively even with an excess of urea. To prepare a concentrated monochlorourea solution, undiluted chlorine water (about $2 \cdot 10^{-2}$ molar concentration, not neutralized) was added with cooling to an equal volume of a urea solution with a molar concentration of urea about 10% above the molar concentration of the chlorine water. The monochlorourea test solutions were then prepared immediately before the tests by appropriate dilution of a freshly prepared chlorourea stock solution with nutrient-depleted Munich tap water. The combined chlorine content was determined by the DPD method according to *Palin* [11]. The UV spectrometric studies showed that in addition to monochlorourea (λ_{max} 200 nm and 244 nm), dichlorourea (λ_{max} 205.5 nm) could have been present only in trace amounts [14]. (In order to rule out the effect of different pH values, all the test solutions used in the studies were adjusted to the pH of Munich tap water, which also was used for the blank determination.)

Experimental setup

The irritant effect of the test solutions on mucous membranes was tested by the method of *Allgayer* and *Korzinek* [5] on rabbit conjunctiva. As mammals, rabbits have an eye that is related to the human eye and about the same size. As "flight animals", they are docile by nature and so are especially well suited for such tests. In order to be able to steadily expose the conjunctiva to the test solutions during the entire testing period, silicone tubing was implanted into the rabbit so that the eye could be constantly wetted without mechanically irritating the eye area or adversely affecting the animal (Fig. 1).

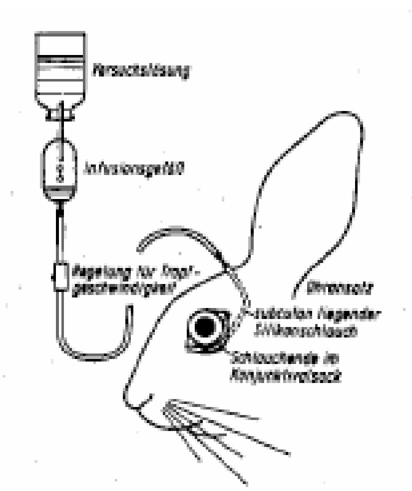

Abb. 1. Schema der Versuchsanordnung.

Fig. 1. Schematic drawing of experimental setup.
KEY:

Test solution

Infusion vessel

Drip rate control

Base of the ear

subcutaneous silicone tubing

End of tubing in the conjunctival sac

The silicone tubing, about 1.5 mm in diameter, was inserted after anesthesia with the help of a cannula from the end of the lacrimal sac near the fold, and run subcutaneously to between the ears. The tubing lay parallel to the conjunctiva in the lower conjunctival sac (Fig. 2) and ended in the inner medial third of the eyelid, without irritating the conjunctiva. The test solutions were fed by means of a standard infusion set that was connected to the silicone tubing between the ears of the animal. The amounts of liquid were kept constant in all the tests and calculated so that the eye was constantly wetted with the test solution, but without ion washout by the (from a physiological viewpoint) relatively ion-poor water. Blinking ensured a uniform distribution of test solution over the entire area of the eye. A test duration of one hour each proved to be appropriate for a comparative assessment. This time period was also accepted by the animals without too much restlessness.

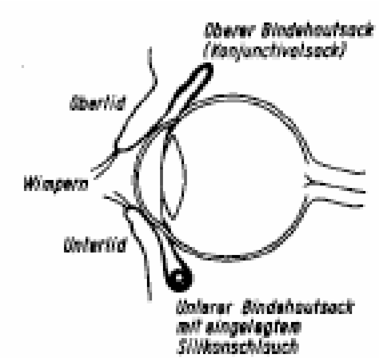

Abb. 2. Lage des Silikonschlauches im unteren Bindehautsack.

Fig. 2. Position of the silicone tubing in the lower conjunctival sac.
KEY:

Upper conjunctival sac

Upper eyelid

Eyelashes

Lower eyelid

Lower conjunctival sac with silicone tubing inserted

The test series was carried out with increasing concentrations until a positive result was achieved, in the sense of objectively detectable irritation of the mucous membranes. Each concentration step for each test solution was tested on 5 to 6 different experimental animals. Assessment was carried out with the help of color photographs taken under standardized conditions, with the rabbit's upper eyelid lifted up from the upper conjunctival sac. The irritant effect was determined only at the upper conjunctival sac, since here any mechanical irritation by the silicone tubing lying in the lower conjunctival sac could be safely ruled out. The pictures were assessed in particular according to the shade of reddening as well as the number and size of the capillaries compared with a blank obtained for the same exposure time with pure Munich tap water.

Results and conclusions

In view of the range to be expected in animal experiments, we feel the test result was surprisingly unambiguous. While for "free chlorine" a clear reaction was first observed at 20 mg/L Cl_2, monochloramine proved to be far more irritating. Thus clear conjunctival irritation could be achieved even with 4 mg/L Cl_2 when it was present in combined form as chloramine; 5 mg/L Cl_2 already produced very severe eye irritation which even spread from the sensitive mucous membranes of the conjunctiva to the less sensitive areas of the ocular membrane. In contrast, the chlorourea solution was somewhat less irritating, but nevertheless its irritant potency was double that of free chlorine. The test results are shown in Table 3.

Table 3. Comparative irritant effects of chlorine, chloramine, and chlorourea solutions on rabbit conjunctiva

	free chlorine in mg/L Cl_2	chloramine in mg/L Cl_2	chlorourea in mg/L Cl_2
no reaction	0-8	0-2	0-6
uncertain reaction	16	3	
clear reaction	20	4	10
severe reaction			12
very severe reaction		5	

As appropriate supplementary tests showed, aqueous ammonium chloride or urea solutions of comparable and even higher concentrations are no different with regard to their irritant effect than Munich tap water, so conjunctival irritation by these substances alone was ruled out.

By means of this series of tests, for the first time in targeted experiments under comparable test conditions, we were able to prove that "free chlorine" and "combined chlorine" have clearly different irritant effects on conjunctiva, and we were able to estimate the relative difference in degree of irritation. Even if the study results are not directly transferable to the human eye and the concentration ratios in swimming pool water, we still can assume that the differences are not fundamental but rather only a matter of degree.

The consequences for treatment, testing, and assessment of swimming pool water that we can draw from the test results are not fundamentally new. Thus previously in the "Guidelines for treatment of swimming pool water" [2], limits were established for "combined chlorine" as a function of the combination of methods and the operating pH, because "combined chlorine" raised doubts about the success of disinfection by chlorination and because even earlier it was suspected that "combined" chlorine was more to blame than "free" chlorine for the irritation symptoms and unpleasant odors observed frequently with chlorination. But these tests certainly provide renewed, experimentally grounded motivation to push for pool water treatment methods aiming to avoid formation of combined chlorine as much as possible, for the restrictions demanded in the "Guidelines" for combined chlorine, and for efforts to develop improved analysis methods for determination of combined chlorine.

Especially since the papers by *Carlson* and *Hässelbarth* [15, 16] we know the importance of a sufficiently high redox potential for the microbial kill rate and thus for the epidemiological quality of pool water. The required values of +700 mV or more can be achieved with even a few tenths of a milligram of "free chlorine" in fresh or well-treated pool water, without the appearance of unpleasant odors or (as we can also deduce from the animal experiments) conjunctival irritation symptoms. However, if higher amounts of combined chlorine are present in the swimming pool water, a germ-free condition can be achieved only with difficulty even with higher free chlorine concentrations; the water could then still be acceptable epidemiologically as necessary, but possibly no longer meets the general hygienic requirements because of the chlorine-nitrogen compounds that are highly irritating and have strong odors. Creating conditions in swimming pool water that are acceptable from an epidemiological and general hygienic standpoint therefore depends to a large extent on whether and to what extent the formation of combined chlorine is stopped or limited to the technically unavoidable concentration. However, this is definitely possible with a swimming pool facility designed and operated according to the state of the art. So chlorine in the pool water does not have to inevitably lead to the irritation symptoms that are of concern, as is commonly assumed. Thus we have established that chlorination, when properly handled, is still an excellent method for treatment and disinfection of swimming pool water that certainly cannot be readily replaced.

We would like to thank the German Research Foundation [Deutsche Forschungsgemeinschaft] for supporting this research.

References

[1] Kroke, R., "Overview of chlorination and treatment of swimming pool water," *Arch. Badew.* **25**, 702-738 (1972) and **26**, 5-37 (1973).

[2] "Guidelines for water treatment for swimming pool water," *Arch. Badew.* **25**, 521-535 (1972).

[3] Mood, E. W., Clark, C. C. and Gelperin, A., "The effect of available residual chlorine and pH upon the eyes of swimmers," *Am. J. Hyg.* **54**, 144-149 (1951).

[4] Voss, H., "Chlorination of swimming pool water and detection of active chlorine," *Arch. Badew.* **19**, 47-49 (1966).

[5] Allgayer, B. "Testing of methods for assessment of the mucosal compatibility of liquids," Medical Dissertation, University of Munich (1975); Korzinek, P., "Development of a method for testing mucosal compatibility of mineral waters by instillation into rabbit conjunctiva," Medical Dissertation, University of Munich (1975).

[6] Hässelbarth, U., "Water hygiene in swimming pools," *Arch. Badew.* **21**, 40-43 (1968).

[7] White, G. C., *Handbook of Chlorination*, 1st ed., Van Nostrand Reinhold Company, New York (1972).

[8] *Geigy Documents - Scientific Tables* [in German], J. R. Geigy AG, Pharmaceutical Division, Basel, 1960.

[9] Palin, A. T., "A study of the chloroderivatives of ammonia and related compounds, with special reference to their formation in the chlorination of natural and polluted waters," *Water and Water Engineering* **54,** 151-159, 189-200, 248-256 (1950).

[10] Lomas, P. D. R., "The combined residual chlorine of swimming bath water," *J. Assoc. Pub. Analysts*, **5**, 27-36 (1967).

[11] Palin, A. T., "Methods for determining free and combined active chlorine, chlorine dioxide, and chlorite, bromine, iodine, and ozone present in water," *Arch. Badew.* **25**, 543-547 (1972).

[12] Kleinberg, J., Tecotzky, M. and Audrieth, L. F., "Absorption spectrum of aqueous monochloramine solutions," *Analyt. Chem.* **26**, 1388-1399 (1954).

[13] Weil, D., "Formation and mode of action of chloramines in drinking water treatment," Dissertation, Technical University of Munich, (1974).

[14] Samples, W. R., "A study on the chlorination of urea," Dissertation, Harvard University, Cambridge, Massachusetts (1959).

[15] Carlson, S. and Hässelbarth, U., "Behavior of chlorine and active oxidizing chloro-substituted compounds in water disinfection," *Vom Wasser*, **35**, 266-283 (1968).

[16] Carlson, S. and Hässelbarth, U., "Determination of the disinfectant effect of chlorinated swimming pool water by measuring the redox potential," *Arch. Hyg.* **152**, 306-320 (1968).