

TECHNICAL NOTE

61 – Combined Chlorine – Understanding it and getting rid of it

December 2020

Combined chlorine levels, which are routinely monitored alongside residual chlorine, are a necessary guide to the health of pool water. This technical note explains the significance of combined chlorine, what do to about excess levels, and how to measure them.

PWTAG recommends that combined chlorine should not exceed 1mg/l. But it does not currently recommend that a pool should necessarily be closed where that level is exceeded. However, such concentrations do indicate a problem that needs analysing and addressing as a matter of priority. It is an indication that the water treatment plant is either having difficulty coping with bather pollution or that detergents in the pool water have combined with chlorine. Either way the bathing conditions are far from ideal, as chlorinous irritants such as dichloramine and nitrogen trichloride will volatise from the water. Pool closure may need to be considered if the issue cannot be resolved in the short term.

Finding the cause

First, it should be established that the design bathing load for the pool is not being exceeded and that the pool water treatment plant is operating in accordance with its design. Second, cleaning material containing detergents (also known as surfactants) may have been used in the vicinity of the pool water. If neither is the case then further checks and remedial action should be taken.

The **free chlorine** should be as low as is consistent with satisfactory microbiological quality – possibly less than 1mg/l in a well-designed and run pool, and with a pH value of 7.2-7.4. In the current COVID-19 pandemic this has now changed to a minimum free chlorine of 1.5mg/l at a pH of 7.0-7.2. (See TN46 on the PWTAG website.)

The **combined chlorine** residual should ideally be zero, certainly no more than half the free chlorine residual – and even if the free chlorine is over 2mg/l, less than 1mg/l. If the combined chlorine is at or above 1mg/l, then further testing should be undertaken to determine the concentration of mono and dichloramines. The procedure for this is detailed below under *Monitoring*.

Dealing with an excess

If the DPD test indicates that the combined chlorine is *mainly monochloramine*, then the free chlorine residual should be re-checked, to make sure it is at the right level. If it is, then the chances are there is too much ammonia, so bathing loads or pollution from bathers may be too high. Or it can indicate that the pool hydraulics are poor; or the turnover period may be too long. If the combined chlorine content is predominately monochloramine it should be reduced by raising the free chlorine to ensure that breakpoint chlorination is being achieved.



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If the pool water treatment system is operating effectively and the design bather load is not being exceeded then monochloramine and dichloramine should, during normal operation, be brought under control in an hour or so by breakpoint chlorination. This is complicated by the slow formation of ammonia from the breakdown of urea, by the recycling nature of the swimming pool water, and continual pool loading. But it should be possible to follow the ratios of combined to free chlorine and draw conclusions accordingly.

For example, if maintaining the correct level of chlorination reduces combined chlorine, the pool water is satisfactory. If increasing free chlorine also increases the combined chlorine, the pool water is unsatisfactory.

If the *monochloramine levels are low*, and the combined chlorine content is predominately dichloramine, then organic chloramines are present. These may arise from bather pollution or reaction with cleaning products incorporating detergents in their formulation. In this case the pool water should be diluted by replacing some of it with fresh make-up water until the combined chlorine is reduced to less than 1mg/l.

A more permanent solution is to use secondary disinfection. Ultraviolet radiation (used alongside a primary disinfectant, usually chlorine) is recommended by PWTAG for its capacity to both reduce chloramines and kill microorganisms – including chlorine-resistant Cryptosporidium. Its use can reduce the chlorine residual levels necessary to keep pool water healthy. It is increasingly used as an alternative to ozone (which similarly complements chlorination) as it is easier and cheaper to fit, especially to existing plant.

Monitoring

Testing for mono and dichloramine to show what combined chlorine is there can be done using a comparator or photometer. The procedures detailed here for both methods will give complete differentiation of the two types of combined chlorine.

Comparator test

- 1. Place a 13.5mm/10ml moulded cell, containing only sample, in the left-hand compartment of the comparator. Rinse out another cell with sample and leave a few drops in the bottom.
- 2. Add to this cell a DPD no1 tablet and crush with a clean stirring rod.
- 3. Add sample to the **10ml mark**. Mix well and place the cell in the right-hand compartment of the comparator. Match the colours immediately (**reading 1**). This reading is the **free chlorine** concentration in mg/l.

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- 4. Add to the right-hand cell a DPD no 2 tablet, mix vigorously to dissolve and match at once (reading 2). The monochloramine concentration is reading 2 minus reading 1.
- 5. Finally, add one DPD no 3 tablet, mix vigorously and allow to **stand for two minutes**. Match against the disc (**reading 3**). The **dichloramine** concentration is **reading 3 minus reading 2**.

Photometer test (Please ensure you follow the manufacturer's instructions for use of the photometer)

- 1. Rinse test cells with sample leaving a few drops in the tube.
- 2. Add one DPD 1 tablet, crush it and then fill the test tube with sample to the **10ml mark**. Mix to dissolve tablet fully and ensure no particles remain.
- 3. Put the lid on the cell and wipe the outside to ensure it is dry.
- 4. Take **photometer reading immediately**, as the result may drift on standing. This is the **free chlorine reading** (**Reading A**).
- 5. Retain test solution and add one DPD 2 tablet, crush and mix to dissolve.
- 6. Put the lid on the cell and wipe the outside to ensure it is dry.
- 7. Take the **photometer reading immediately** (**Reading B**). **Reading B** less **Reading A** is the **monochloramine** concentration as mg/l (ppm) Cl2.
- 8. Retain the test solution and add one DPD 3 tablet, crush and mix to dissolve. **Stand for two minutes** to allow full colour development.
- 9. Put the lid on the cell and wipe the outside to ensure it is dry.
- 10. Take the **photometer reading (Reading C**). **Reading C** less **Reading B** is the **dichloramine** concentration as mg/l (ppm) Cl2.
- 11. Don't forget to rinse and clean all cells immediately.

Whether or not you are using a comparator of photometer please ensure that the cells for the tests are labelled and kept separately and the specific cells for the test are utilised. Take care to observe whether or not bleaching out is occurring when the DPD 1 tablet is added to the small amount of water in the tube. If it is then a dilution test will be required first, prior to undertaking the further tests.