Environmental Public Health Division
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HOW TO SHOCK THE POOL
(CHLORINATE TO BREAKPOINT)

Chloramines / Combined Chlorine

If you smell "chlorine", coming from your pool, what you really smell are combined forms of chlorine, also called chloramines. Chloramines are chemical compounds formed by chlorine combining with nitrogen containing contaminates in the pool water. These are still disinfectants, but they are 40 to 60 times less effective than free available chlorine. Contaminates come from swimmer wastes such as sweat, urine, body oil, etc. Therefore, requiring all bathers to take a warm, soapy water shower is a good idea.

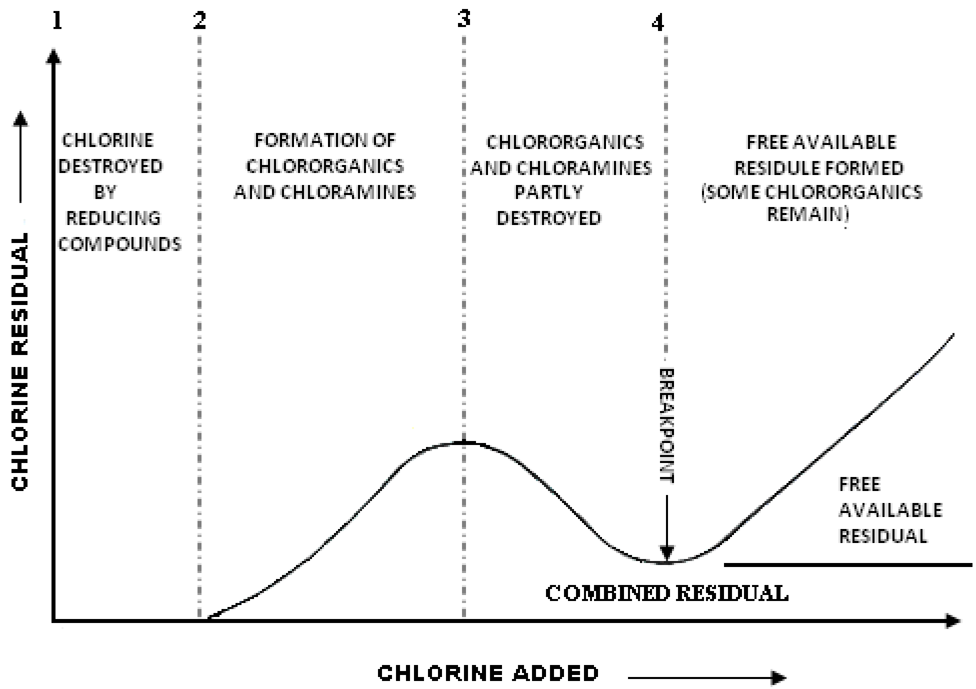
Three types of chloramines can be formed in water - monochloramine, dichloramine, and trichloramine. Monochloramine is formed from the reaction of hypochlorous acid with ammonia. Monochloramine may then react with more hypochlorous acid to form a dichloramine. Finally, the dichloramine may react with hypochlorous acid to form a trichloramine. Trichloramines cause the "chlorine" smell and hang in the air directly above the pool water level, often causing competitive or frequent swimmers to have asthma like symptoms. High levels of chloramines will also cause corrosion to surfaces and equipment in the pool area. The trichloramines are especially irritating to the eyes, nose and lungs.

Chloramines can usually be eliminated from the pool water by performing breakpoint chlorination with chlorine or super oxidation with a non-chlorine oxidizer. Ultraviolet systems and ozone systems are effective at reducing chloramines in pools.

Breakpoint chlorination

Break point chlorination is adding enough chlorine to eliminate problems associated with combined chlorine. Specifically, breakpoint chlorination is the point at which enough free chlorine is added to break the molecular bonds, specifically the combined chlorine molecules, ammonia or nitrogen compounds. It takes a ratio of chlorine to ammonia atoms of 7.6 to 1 to reach breakpoint, other contaminants (i.e., bacteria, algae) are also present that must be oxidized, so 10 times the amount of combined chlorine must be added. When sufficient free chlorine (FC) is added to pool water, the inorganic chloramines are converted to dichloramine, then to nitrogen trichloride, and then to nitrogen gas. Any excess chlorine leftover will become the chlorine residual (FC).

The graph below shows what happens when chlorine (either chlorine gas or a hypochlorite) is added to water. First (between points 1 and 2), the water reacts with reducing compounds in the water, such as hydrogen sulfide. These compounds use up the chlorine, producing no chlorine residual.



Between points 2 and 3, the chlorine reacts with organics and ammonia naturally found in the water. Some combined chlorine residual is formed – chloramines.

Between points 3 and 4, the chlorine will break down most of the chloramines in the water, actually lowering the chlorine residual.

Finally, the water reaches the breakpoint, shown at point 4. The breakpoint is the point at which the chlorine demand has been totally satisfied - the chlorine has reacted with all reducing agents, organics, and ammonia in the water. When more chlorine is added past the breakpoint, the chlorine reacts with water and forms hypochlorous acid in direct proportion to the amount of chlorine added.

The combined chlorine (CC) level is calculated by subtracting the free chlorine (FC) from the total chlorine (TC) in the pool/spa water. Rule 410 IAC 6-2.1-30(o) 2 requires testing of the pool/spa water for combined levels at least twice a week.

Rule 410 IAC 6-2.1-30(e) requires "The pool water shall be superchlorinated to breakpoint or superoxidized with a nonchlorine oxidizer, when the pool test kit reveals a combined chlorine (chloramine) concentration of five-tenths (0.5) parts per million (ppm) or greater." However, studies have shown that swimmers find pool water the most enjoyable if more than 85% of the total chlorine is free chlorine. Therefore, the Environmental Public Health Staff recommends superchlorination when the combined chlorine concentration is 0.2 ppm or greater (a total chlorine of 1.2 ppm and a free chlorine of 1.0 ppm provides 83% of total chlorine as free chlorine).

Note: Pools using bromine as a sanitizer must also perform breakpoint superchlorination using chlorine. Like chlorine, bromine combines with organic impurities to form combined bromine and bromamines.

For a more complete discussion of breakpoint chlorination see the North South Wales, Australia health website: https://www.health.nsw.gov.au/environment/factsheets/Pages/breakpoint-chlorination.aspx or the addendum to this document.

Achieving Breakpoint Chlorination

To achieve the breakpoint, the free chlorine (FC) added to the water must be about ten times the amount of combined chlorine (CC). This is an "all or nothing" process. Not adding enough chlorine to reach breakpoint will make the problem even worse as the result is the formation of more chloramines and re-dissolving of chloramines back into the pool water. Continual "shocking" but not reaching breakpoint will result in the pool reaching a point of no return. Partial or complete draining of the pool water and refilling with fresh water may be the only remedy at this point. If an indoor pool facility has inadequate air exchange with outdoor fresh air, it will be necessary to add air circulation fans with doors and windows open to keep the air above the pool water level moving to prevent re-dissolving of nitrogen (by product of breakpoint chlorination) leading to more chloramine formation.

Please note as required in 410 IAC 6-2.1, Sec. 30 (g) "The pool shall be closed and remain closed during breakpoint chlorination" and adding too much chlorine, beyond breakpoint, will yield high chlorine residual that may require the pool to remain closed until the free chlorine residual drops to an acceptable level as required in 410 IAC 6-2.1, Sec. 30 (b).

Calculating Amount of Chemical to Achieve Breakpoint Chlorination

The DPD test does not measure combined chlorine (CC) directly, it measures free chlorine (FC) in Step 1 and total chlorine (TC) in Step 2. Total Chlorine is the sum of free chlorine and combined chlorine. Therefore, combined chlorine is the difference between total chlorine and free chlorine. CC = TC – FC.

The first step in determining the necessity of a shock treatment is to determine the level of combined chlorine.

Using the D.P.D. testing kit, test for free chlorine (FC) and total chlorine (TC). After completing the water test, you subtract the free chlorine reading from the total available chlorine reading, the result indicates the combined chlorine (CC) or chloramine level in the pool water.
For example:
Combined Chlorine = Total Chlorine - Free Chlorine
2.3 ppm (TC) measured from test kit - 1.5 ppm (FC) measured from test kit = 0.8 ppm CC.

If the water has no chloramines, the answer to the subtraction will be zero (0) and a shock treatment is not needed. This is a desirable level. After determining the level of combined chlorine in the pool water, the pool operator must determine the breakpoint chlorination for that value.

The breakpoint chlorination value is 10 times the combined chlorine (CC) level.
For example: 0.8 ppm (CC) from the above example × 10 = 8 ppm of chlorine to achieve breakpoint. Taking into account the free chlorine already in the pool, chlorine will have to be added to the level of 8 ppm.

Determine the Amount of chemical to add*:

Example**: Calculate the chemical change to achieve Breakpoint Chlorination in 60,000-gallon pool with FC of 1.5 ppm and TC of 2.3 ppm. Using 67% Calcium Hypochlorite where the label states that 2 oz will produce a chemical change of 1ppm in 10,000 gallons of water:

STEP 1: Determine the amount of Combined Chlorine (CC)

Total Chlorine (TC) – Free Chlorine (FC) = Combined Chlorine (CC)

2.3 ppm – 1.5 ppm = **0.8 ppm**

STEP 2: Calculate the breakpoint Chlorination (BPC) amount

Breakpoint (BPC) = CC × 10

0.8 × 10 = **8.0 ppm**

STEP 3: Determine the desired change amount

Desired Change = BPC – FC

8.0 ppm – 1.5 ppm = **6.5 ppm**

STEP 3: Determine the amount of chemical to add:

Amount of chemical from product label	**Actual Pool Volume**	**Desired Chemical Change**	**Total**
	60,000	6.5	
	÷ 10,000 from product label	÷ 1.0 ppm from product label	
2 oz.	× 6	× 6.5	78 oz

Convert answer to pounds: 78 ÷ 16 = 4.875 lbs.; rounded to 5 pounds.

Steps 1 must be done using a DPD test, using the test kit instructions.

*For an alternate and somewhat simpler method for calculating chemical amounts for breakpoint chlorination see the addendum to this document.

**For additional information on calculating chemical amounts to add to pools see: www.in.gov/isdh/files/Chemical_adjustment_pool.pdf

Stabilized chlorine compounds, such as DICHLOR or TRICHLOR may not be used for "shocking" because the permitted level of cyanuric acid would be exceeded over the season. It also would cause the water to have elevated chlorine levels for days.

NON-CHLORINE OXIDIZERS

Non-chlorine oxidizers may be used instead of chlorine breakpoint chlorination, but the pool will still have to be superchlorinated periodically with a chlorine compound to kill off the bacteria that become resistant to constant exposure to low levels of disinfectant (chlorine or bromine). Non-chlorine oxidizer products will oxidize or destroy ammonia, nitrogen and some swimmer waste, but will not kill bacteria or algae.

Although an advertised advantage to using a non-chlorine oxidizer is the shut down time may be as little as one half-hour; 410 IAC 6-2.1-30(s) requires that "The pool shall be closed for a period equal to at least one (1) hour following the manual addition of chemicals."

If the manufacturer's label requires closure for more than one hour, then 410 IAC 6-2.1-30(h) states that "… the pool shall be closed and shall remain closed in accordance with the specifications on the product label."

Potassium monopersulfate is the ingredient used in most non-chlorine oxidizers. As an oxidizer, it reacts with contaminants and prevents combined chlorine from forming (short term). The use of potassium monopersulfate will result in false readings of chlorine for up to 6 hours as it oxidizes the iodide in the reagent as if it were combined chlorine. There is a reagent available to correct this.

The use of non-chlorine shock chemicals will also interfere with oxidation reduction potential (ORP) readings because it measures the oxidizing potential of the water. These products are an oxidizer causing high ORP readings, but again it is not a disinfectant. In the end, the required free chlorine residual level for disinfection in the pool water may be below the required level as stated in 410 IAC 6-2.1.

Other options:

1. Adding a medium pressure UV (ultraviolet) light or ozone system to eliminate chloramines in the pool water. Many large indoor pools used for competition (i.e. colleges and high schools) have had success with using UV. Please note, in the State of Indiana, either system can only be permitted as supplemental disinfection to chlorine disinfection.

2. In addition to the disinfection of bacteria and viruses, UV-C will oxidize chloramines. UV-C that is used for chloramine destruction in indoor pools and spas must be polychromatic that produces wavelengths of 200-350 nanometers with a minimum dosage (fluence) of 600 J/m2 (60 mJ/cm2). Multiple wavelengths are necessary to destroy chloramines as listed below:

Monchloramine	245 nanometers
Dichloramine	297 nanometers
Trichloramine	260 and 340 nanometers

3. Some municipal water companies are using chloramines for additional disinfection in the distribution system, so there may be significant background levels in the pool supply water. In this case, carbon filters may be an option to reduce the chloramines in the source water.
4. Increasing the amount of fresh water added daily to the pool.
5. For spas, it may be best to drain and refill with fresh water more often. Recommended drain and refill calculation is: Spa gallons ÷ 3 ÷ users per day = replacement interval (days).

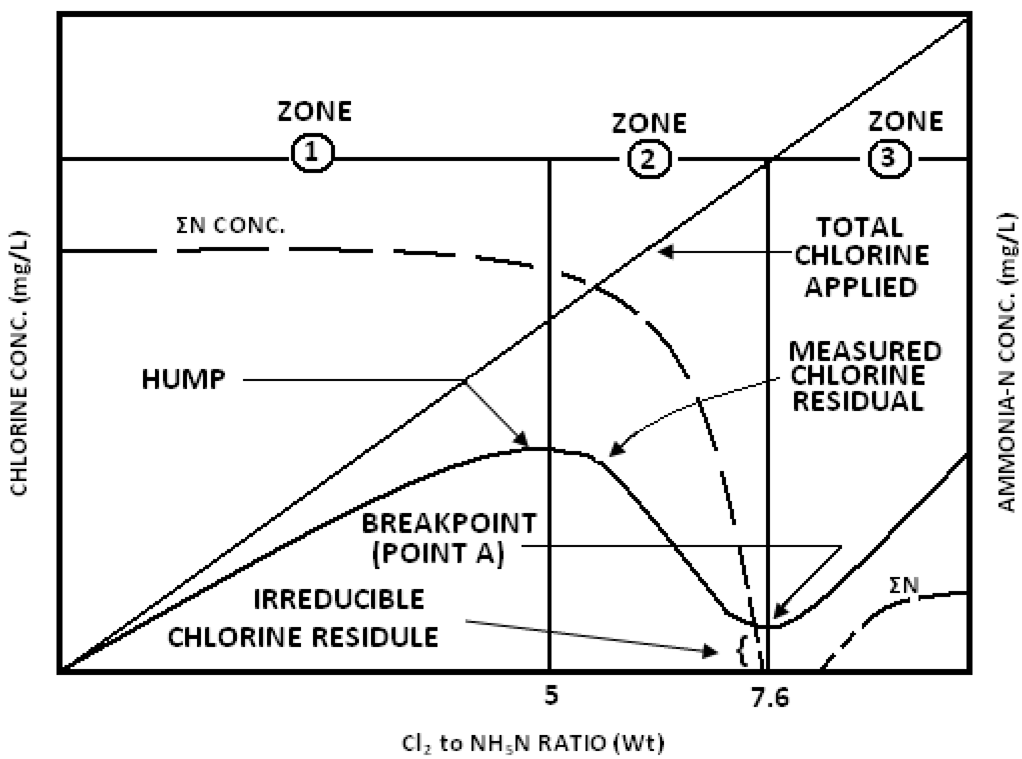
The science behind the chloramine production is evolving and as science adds to the knowledge, this document will be changed, as appropriate, to reflect those improvements. For the most up to date information on chloramines in indoor swimming pools see the Environmental Public Health Division's swimming pool web page at www.pools.isdh.in.gov.

Other resources about indoor air irritants and break point chlorination:

www.cdc.gov/healthywater/swimming/pools/irritants-indoor-pool-air-quality.html
https://www.health.nsw.gov.au/environment/factsheets/Pages/breakpoint-chlorination.aspx
www.in.gov/isdh/files/Chemical_adjustment_pool.pdf

Addendum

‚Breakpoint Chlorination*
Graphical Representation of Breakpoint Chlorination



The above graph demonstrates the theory of continuous breakpoint chlorination. On the left vertical axis is the chlorine concentration in mg/L which is zero at the bottom of the axis and increases with height. On the right vertical axis is the ammonia-nitrogen (i.e. ammonia measured as nitrogen) concentration also in mg/L which is zero at the bottom of the axis and increases with height. The bottom horizontal axis represents the ratio of chlorine (Cl_2) to ammonia (NH_3) by weight which is zero on the left and increases to the right. The bottom horizontal axis also represents time and increases from left to right. There are three inter-related lines on the graph:

- ΣN CONC.: (sigma ammonia-nitrogen concentration) represents the concentration of the sum of all forms of ammonia-nitrogen in the pool.
- Total Chlorine Applied: the constant dose of chlorine being introduced into the pool.

- Measured Chlorine Residual: the measured total chlorine residual in the pool.

The breakpoint curve is a graphical representation of chemical relationship that exists with constant addition of chlorine to swimming pool water containing a small amount of ammonia-nitrogen. This graph represents a swimming pool where bathing has ceased, and no further ammonia-nitrogen is introduced into the pool. During an overnight period, sodium hypochlorite is added at a constant rate. This curve has three zones.

Zone 1

Staring from the left side of the graph; there is already a concentration of ammonia-nitrogen (ΣN CONC) in the pool from bathers. Chlorine has been allowed to fall to zero and Total Applied Chlorine and Measured Chlorine Residual are both zero. Chlorine is then added at a constant rate. The principal reaction in Zone 1 is the reaction between chlorine and the ammonium ion. This reaction results in a Measured Total Chlorine of only monochloramine to the hump in the curve. The hump occurs, theoretically, at chlorine to ammonia-nitrogen weight ratio of 5:1. This ratio indicates the point where the reacting chlorine and ammonia-nitrogen molecules are present in solution in equal numbers. Monochloramine does not readily degrade.

Zone 2

The breakpoint phenomenon occurs in this zone which is also known as the chloramine destruction zone. As the weight ratio exceeds 5:1, some of the monochloramine starts reacting with further addition of chlorine to form dichloramine, which is about twice as germicidal as monochloramine. A pure dichloramine residual has a noticeable disagreeable taste and odor, while monochloramine does not. Total Chlorine Applied is still increasing and both the Concentration of ammonia-nitrogen and Measured Chlorine Residual decrease rapidly. This rapid decrease occurs because the dichloramine is reacting immediately with additional hypochlorous acid in a series of destruction reactions to form volatile compounds and other by-products such as nitrogen gas, nitrate and chloride. Therefore, ammonia and chlorine are consumed in the reactions and lost from the pool. Thus, additional chlorine is required to destroy ammonia and chloramines.

The breakpoint (Point A) is the point of the lowest concentration of Measured Chlorine Residual where nuisance chlorine residuals remain and where ammonia-nitrogen is not detected. The nuisance chlorine residuals are mainly organic chloramines which cannot be oxidized any further by reacting with hypochlorous acid.

Zone 3

Zone 3 is to the right of the breakpoint (Point A) and is where a free chlorine residual will appear. The total residual consists of the nuisance residuals plus free chlorine. If trichloramine is formed, it will appear in this zone. In practice it has been found the most pleasant water for bathing will occur if more than 85% of the total chlorine is free chlorine.

In reality, ammonia-nitrogen does not stay static but is continually added while the pool is open to the public. **To achieve breakpoint chlorination, chlorination must continue after the pool has been closed to the public to ensure oxidation of the additional chloramines.**

The shape of the breakpoint curve is affected by contact time, temperature, concentration of chlorine and ammonia, and pH. Higher concentrations of the chemicals increase the speed of the reactions.

*From https://www.health.nsw.gov.au/environment/factsheets/Pages/breakpoint-chlorination.aspx

Alternate Method for Calculating Chemical Additions to Achieve Breakpoint*

The formula for breakpoint chlorination using LIQUID chlorine (sodium hypochlorite):
Volume of the pool in gallons, times 8.3 (weight of one cubic ft. water), times the combined chlorine level (total chlorine minus the free available chlorine) times 1.0 (lbs. of chlorine in one gallon of liquid chlorine) times 10 (ten times combined chlorine level) divided by one million to calculate the amount of gallons of chlorine needed to reach breakpoint chlorination.

(POOL VOLUME (in gallons) × 8.3 × Combined Chlorine × 1.0 × 10) ÷ 1,000,000 = Gallons of sodium hypochlorite (12%) needed to reach breakpoint chlorination

Example: Calculate the chemical change to achieve Breakpoint Chlorination in 60,000 gallon pool with FC of 1.5 ppm and TC of 2.3 ppm. Using 12% Sodium Hypochlorite

STEP 1: Determine the amount of Combined Chlorine (CC)

Total Chlorine (TC) – Free Chlorine (FC) = Combined Chlorine (CC)

2.3 ppm – 1.5 ppm = **0.8 ppm**

STEP 2: Determine the amount of chemical to add:

Actual Pool Volume	**Weight of one Gallon of Water**	**Combined Chlorine**	**Lbs. of chlorine in 1 gallon**	**10 Times CC Level**	**Divide by one million**	**Total**
60,000	× 8.3	× .8	× 1	× 10	÷ 1,000,000	4 gallons

Step 1 must be done using a DPD test, using the test kit instructions.

In this example, 4 gallons of sodium hypochlorite is needed to properly reach breakpoint chlorination.

NOTE: When shocking a pool, the chlorine-based chemical used for shocking the water must be added all at once so that the concentration throughout the pool reaches breakpoint chlorination.

The formula for breakpoint chlorination using granular chlorine (calcium hypochlorite) is:
Volume of pool water in gallons times 8.3 (weight of one cu. ft. of water) times combined chlorine (CC) level (total chlorine minus the free available chlorine, determined from the D.P.D. test kit) times 1.5 lb. (weight of one pound of calcium hypochlorite) times 10 ppm representing 10 new, free available chlorine parts per million. Divide all the above by 1,000,000 to determine breakpoint in pounds of granular chlorine (calcium hypochlorite 67%) needed.

POOL VOLUME (in gallons) × 8.3 × COMBINED CHLORINE x 1.5 × 10 ÷ 1,000,000 = Free chlorine residual needed to reach breakpoint chlorination in pounds of granular chlorine

Example: Calculate the chemical change to achieve Breakpoint Chlorination in 60,000 gallon pool with FC of 1.5 ppm and TC of 2.3 ppm. Using 67% Calcium Hypochlorite

STEP 1: Determine the amount of Combined Chlorine (CC)

Total Chlorine (TC) – Free Chlorine (FC) = Combined Chlorine (CC)

2.3 ppm – 1.5 ppm = **0.8 ppm**

STEP 2: Determine the amount of chemical to add:

Actual Pool Volume	Weight of one Gallon of Water	Combined Chlorine	Weight of Calcium Hypochlorite	10 Times CC Level	Divide by one million	Total
60,000	× 8.3	× .8	× 1.5	× 10	÷ 1,000,000	6 Lbs.

Step 1 must be done using a DPD test, using the test kit instructions.

In this example, 6 pounds of calcium hypochlorite is needed to properly reach breakpoint chlorination.

*These calculations assume a free chlorine level of 0.0 ppm. They may leave a higher concentration of free chlorine after reaching breakpoint, but will ensure that breakpoint is reached.

For additional information on calculating chemical amounts to add to pools see: www.in.gov/isdh/files/Chemical_adjustment_pool.pdf