

# Taylor Technologies'

## *Chemistry Topics*

*Reader note: Available on-line at [http://taylortechnologies.com/learnmore\\_chemistry.asp](http://taylortechnologies.com/learnmore_chemistry.asp)*

### 1. REAGENT SHELF LIFE

### 2. UNDERSTANDING CALCIUM HARDNESS

### 3. PUTTING FAS-DPD TO THE TEST:

### 4. "SHOCKING" INTERFERENCE

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## REAGENT SHELF LIFE

All reagents have a shelf life, whether they are liquids, powders, crystals, tablets, or test-strip pads. If kept dry, powders and crystals are very stable; acids are also long lived. Date of manufacture is not the controlling factor when it comes to shelf life—storage conditions are more important. **As with all perishables, reagents are sensitive to environmental influences and will last longer under controlled conditions.**

To this end, we recommend:

- Storing reagents at a consistent temperature in the range of 36°–85°F (2°–29°C); extreme temperature fluctuation, say from a refrigerator to a hot car trunk, causes reagents to deteriorate.
- Keeping them out of prolonged direct sunlight. (Note: their brown plastic bottles help protect very light-sensitive reagents.)
- Segregating reagents from containers of treatment chemicals.
- Replacing caps immediately and tightening them carefully so that exposure to air and humidity is limited.
- Avoiding switching bottle caps, placing bottle caps on soiled surfaces, re-pouring reagents into contaminated containers, or touching test strip pads.

Taylor formulates its reagents to remain effective for at least one year, with only very few exceptions (molybdenum indicator in liquid form is one; after four months old it should be tested against a standard periodically). **As a general precaution, replace all reagents more than one year old, or at the beginning of a new testing season.**

# **UNDERSTANDING CALCIUM HARDNESS**

Calcium hardness must be actively managed—along with pH and total alkalinity—to keep water in proper chemical balance. Current industry standards call for maintaining calcium hardness in the ideal range of 200–400 ppm in pools and 150–250 ppm in spas.

## **The Role of Calcium Hardness in Water Balance**

While hardness in water consists of both calcium and magnesium salts ("total hardness"), only the calcium component is relevant in the water balance calculation for pools and spas. Called the Saturation Index (SI) formula, it considers the interrelationships of four chemical factors—calcium hardness; pH; total alkalinity, as corrected for the contribution of any cyanuric acid stabilizer in use; and, to a much lesser extent, the total dissolved solids level—plus one physical factor, water temperature. All but the mathletes among us use a water balance calculator like Taylor Technologies' Watergram® to do the number crunching involved. The value one arrives at reflects the water's degree of saturation with calcium carbonate.

When the SI value is zero, the water is properly balanced. Its calcium hardness, pH, and total alkalinity are acting in harmony with one another. When the SI is +0.5 or more, the unbalanced water is trending toward scaling, meaning conditions are right for calcium carbonate to come out of solution and deposit on surfaces as "scale." When the SI is -0.5 or less, the unbalanced water is trending toward corrosivity. Corrosive water attacks plaster, concrete, grout, and metal, resulting in etching, pitting, and surface stains and/or colored water caused by metal pulled out of piping, fittings, and equipment.

Can damage from scaling water be reversed? By reducing the SI to around -1.0 for a short time (usually by lowering pH), some calcium deposits in the filter and circulation piping can be dissolved, and the water's flow may even remove chunks of loosened scale. But this will come at a price. A thin layer of the concrete surface of the pool may dissolve as well, and copper can be lost from piping and/or heat exchangers.

Damage from corrosive water cannot be reversed, only repaired by resurfacing the concrete and replacing piping. Colored water can be cured with a "metal out" product, or chelating agent, and some of these are reportedly successful at removing certain surface stains.

## **The Effects of High and Low Hardness**

Specifically, water with high calcium hardness gets cloudy unless the alkalinity and/or pH are low enough to compensate. As mentioned, the excess calcium carbonate will precipitate as crusty, grayish white scale on surfaces, piping, and equipment. It's unsightly, can cause abrasions on users and snag bathing suits, and makes a good anchor for microorganisms. It will clog filters. When it builds up in piping, circulation is reduced and pressure increases. Scaling is an especially acute problem in heaters because calcium's solubility is inversely proportional to temperature: as temperature increases, less calcium is able to stay dissolved. Scale on the pipes or coils acts as an insulator, slowing heat transfer. This makes it more expensive to heat the water. Over time, thick scale will cause a heater to fail.

Water with low calcium hardness will seek more by dissolving it from surfaces it comes in contact with that contain calcium, such as plaster, grout, and concrete decking. The late Dr. Neil Lowry, a

well respected instructor in our industry, preferred to call water with low calcium hardness "aggressive" rather than "corrosive" because the latter term implies the destruction of metals. He would point out that copper water pipes in homes equipped with water softeners last for decades! The corrosiveness of unbalanced water, he would tell his students, comes from poorly maintained alkalinity and pH.

Calcium Hardness Too Low	Calcium Hardness Too High
<ul style="list-style-type: none"> <li>• pitting of concrete pool surfaces</li> </ul>	<ul style="list-style-type: none"> <li>• cloudy water</li> </ul>
<ul style="list-style-type: none"> <li>• etching of plaster</li> </ul>	<ul style="list-style-type: none"> <li>• rough surfaces</li> </ul>
<ul style="list-style-type: none"> <li>• dissolving of grout</li> </ul>	<ul style="list-style-type: none"> <li>• clogged filters and reduced circulation through piping</li> </ul>
<ul style="list-style-type: none"> <li>• pitting of concrete pool deck</li> </ul>	<ul style="list-style-type: none"> <li>• heater inefficiency</li> </ul>

## Testing

To avoid damage to pools and spas from unbalanced water, test calcium hardness at least monthly. Calcium hardness is best monitored with a drop-count titration, as test strips can only measure total hardness. In addition, whereas test strips for total hardness have just four or five color blocks to cover a tremendously wide range—from 0 to 1,000 parts per million (ppm) with color blocks for 0, 100, 250, 500, 1,000, for instance—a drop test will allow you to approach the true concentration of calcium hardness in 10-ppm increments. This means if you're faced with wanting to balance water in a spa by increasing the calcium hardness from 60 ppm to 150 ppm, the strip can't help but the drop test can.

To perform a drop test, simply fill a test cell with sample water, add buffer and indicator reagents, and swirl to mix. The sample will turn red if calcium hardness is present. Next, add the calcium hardness reagent, swirling and counting each drop, until the color changes from red to blue. Finally, multiply the number of drops used by the equivalence factor in the test instructions to determine the calcium hardness level. The reading is expressed as parts per million of calcium carbonate.

Note: retailers with water-testing stations may find that using a countertop laboratory with a built-in magnetic stirrer speeds up performance.



*The color progression in a hardness test is from red, to a mixture of red and blue, to blue. To be certain the color change is permanent, indicating you have reached the true endpoint, add one more drop of titrant. If the blue color remains unchanged, do not count this drop.*

## **Beware the Fading Endpoint**

Occasionally when testing calcium hardness you may get a purple endpoint instead of blue. This is called a "fading endpoint" and is due to interference from metal ions (most likely copper from algaecides, pipes, or source water). Retest, but prevent the interference by adding five or six drops of hardness reagent to the sample before adding the buffer and indicator. Then proceed as usual. Remember to count the drops of titrant added at the beginning when you calculate the total number of drops required to reach the endpoint.

## **Adjusting Hardness**

You can raise water's calcium hardness easily by adding calcium chloride ( $\text{CaCl}_2$ ). Two forms are sold: hydrated (77% strength) and anhydrous (100% strength). Each will generate heat when contact with water is made. Therefore, generally you are instructed NOT to pre-dissolve the calcium chloride in a bucket, but to broadcast it over the water's surface with the pump running. Adding calcium chloride in the hours before or after treating with soda ash (sodium carbonate) or baking soda (sodium bicarbonate) will result in cloudy water.

To decrease calcium hardness, you must partially drain the vessel and refill it with lower-hardness water. Unless pH and alkalinity are already low, however, it will often be more practical to adjust the Saturation Index by lowering these two factors through the addition of acid than to replace water. This would certainly be the case where drought has caused limits to be placed on water used for recreation.

# PUTTING FAS-DPD TO THE TEST: THE LATEST TREND IN CHLORINE ANALYSIS

Since the 1970s, most professionals monitoring water quality in pools and spas have used one of two methods to analyze chlorine levels: **OT** (orthotolidine), which produces a yellow color in the sample, or **DPD** (N, N-diethyl-p-phenylenediamine), which produces a pink color. Using OT, one can only measure total chlorine—the sum of active plus spent sanitizer—making it impossible to determine whether an adequate residual exists to disinfect the water. Because of this, health departments in the United States now do not permit the use of OT at regulated facilities.

DPD chemistry can distinguish the active sanitizer, termed free available chlorine. When DPD in either liquid or tablet form is added to a water sample, a pink color forms with an intensity proportional to the chlorine concentration (either free or total, depending on the step you're on in the procedure). The color of the treated sample is then compared to a set of color standards supplied by the test kit manufacturer. These standards may be encapsulated liquid dyes, colored plastic, printed colors on clear film, or printed colors on paper.

Subtracting the free chlorine reading from the total chlorine reading yields the amount of combined chlorine in the water. Combined chlorine, an ineffective sanitizer, causes eye and mucous membrane irritation and the so-called "chlorine odor" associated with poorly maintained pools. Combined chlorine is eliminated by superchlorinating to the breakpoint dosage. Calculations for breakpoint dosage depend on knowing the amount of combined chlorine in the water, which is why DPD is superior to OT for testing chlorine-sanitized pools.

The latest trend among service professionals and a significant number of health officials is testing chlorine with **FAS-DPD**. This variation of the traditional DPD method allows users to measure both free and combined chlorine levels as low as 0.2 ppm—the maximum allowable level for combined chlorine according to most health authorities as well as the Association of Pool & Spa Professionals (ANSI/APSP)—and as high as 20 ppm. By contrast, the color comparators used with the standard DPD test generally allow readings at the low end of 0.5 and 1 ppm and at the high end of 5 or maybe 10 ppm.

An **FAS-DPD** titration is as simple as a test for total alkalinity or calcium hardness. A buffered DPD indicator powder is added to a water sample and reacts with chlorine to produce the pink color characteristic of the standard DPD test. Ferrous ammonium sulfate (FAS) is then added drop by drop until the pink color completely and permanently disappears, signaling the endpoint of the reaction. To get the reading, the number of drops used to cause this color change is multiplied by the appropriate factor for the size of the water sample (supplied by the manufacturer).



The distinct change from a vibrant pink to no color at all eliminates the need for color matching. This means when testing samples with a high level of sanitizer, the user does not have to distinguish between relatively close gradations of color or be concerned that any color has been bleached out of the sample. It is also a boon to the six to eight percent of the population with red-green deficiencies in their color vision (mainly men).

The second part of the FAS-DPD test determines the amount of combined chlorine present (i.e., mono-, di-, or trichloramines) by the number of drops needed to turn the sample from vibrant pink to colorless again.

Not everyone who tries it makes a complete switchover. The cost per test is a little higher and the procedure takes a bit longer. But almost everyone who tries FAS-DPD keeps it on hand for troubleshooting problem pools or use by the "color challenged."

Taylor offers FAS-DPD in several combination kits and as a stand-alone test:

[See all pool/spa kits with FAS-DPD.](#)

[See all industrial kits with FAS-DPD.](#)

*Reader note: This article about how to accurately measure chlorine levels in water shocked with potassium monopersulfate originally appeared in Aquatics International and was reviewed before publication by Edward Lightcap of DuPont.*

## "SHOCKING" INTERFERENCE

The most popular sanitizers used in pools and spas—chlorine and bromine—function both as biocides (they kill bacteria and other potentially harmful microbes) and oxidizers (they "burn up" unpleasant organic contaminants like bather wastes, dust, and pollen). In a heavily used pool, as much as 90% of the chlorine or bromine may be working to eliminate organic impurities. This ratio is unwise. Periodic addition of a supplemental oxidizer—a "shock treatment"—can free up the sanitizer for its highest purpose, germ killing. A popular choice is a non-chlorine shock with potassium monopersulfate as the active ingredient. (The label may also call it potassium peroxymonosulfate.)

Potassium monopersulfate is a powerful oxidizer with several attractive properties (see sidebar). Properly applied, it will cleanse water in short order, without raising the chlorine level or creating combined chlorine. Bathers can re-enter the water after waiting only one hour to allow proper mixing and circulation. The reaction byproducts are harmless sulfate salts. Monopersulfate does have one drawback when used in chlorinated pools: it can interfere with the combined chlorine reading obtained with DPD and FAS-DPD tests. Some pools even have been closed because of supposed high combined chlorine (chloramine) readings when, in fact, the high readings were the result of this test interference.

### Chlorine test interferences

Commercial operators are generally required by regulatory authorities to use a DPD test to monitor chlorine. Kits for this purpose may employ liquids, tablets, a powder, or a combination of these forms, depending on the manufacturer. The test method can involve either color matching (the pink color that develops in the treated water sample is proportional to the amount of chlorine present; the reading is determined by matching the pink to a set of color standards), or counting drops (the treated water sample goes from pink to colorless upon the addition of a titrating reagent, and the number of drops used determines the amount of chlorine present). The reagent all the best selling kits have in common is DPD #3. DPD #3 contains potassium iodide. Monopersulfate shocks will react with the potassium iodide in DPD #3, making it seem there is a higher combined chlorine level in the water than there actually is.

Here are two typical scenarios:

In the standard color-matching DPD test, you first add DPD #1 and DPD #2 to your water sample to develop a pinkish-red color proportional to the level of free chlorine. After taking that reading, you add DPD #3 to obtain the total chlorine level. You then calculate the amount of combined chlorine by subtracting free from total chlorine.

$$\text{Combined Chlorine} = \text{Total Chlorine} - \text{Free Chlorine}$$

When monopersulfate is present in the sample, it reacts with DPD #3 in the total chlorine test, producing a dark pink/red color characteristic of a high total chlorine reading. However,

monopersulfate will not react with the DPD #1 and #2 reagents used to measure free chlorine. Therefore, the combined chlorine level obtained doing the calculation above is artificially high.

In an FAS-DPD drop-count titration, you add DPD indicator powder to the water sample and it will turn pink if free chlorine is present. Next you add FAS-DPD titrating reagent drop by drop until the sample changes from pink to colorless. You then multiply the number of drops added by an equivalence factor (stated in the test instructions) to get the free chlorine reading. Finally, you add DPD #3 reagent to the treated sample, which will turn pink if combined chlorine is present. Once again, you titrate until the sample turns colorless and multiply the drop count by the given equivalence factor to get the combined chlorine reading. If monopersulfate is present in the sample it will react with DPD #3, artificially increasing the combined chlorine reading.

## Preventive measures

To get an accurate combined chlorine reading, commercial operators have two options: 1) shock in the evening and wait at least eight hours afterward before testing or 2) if shocking is required before or during the hours of operation, use a test kit with reagents that can eliminate the interference. There are kits on the market that include a neutralizing agent for monopersulfate along with the standard chlorine test reagents, or the neutralizer can be purchased separately. You simply add the neutralizer as instructed then take the readings as you normally would.

Should you wish to measure monopersulfate concentrations, take a fresh sample and perform the chlorine tests a second time without masking the interference. The result will be the total amount of oxidizer in the water. Subtract the total chlorine reading obtained in the first test from this total oxidizer reading to find the level of monopersulfate. *Note:* This will give a monopersulfate reading in ppm as chlorine. To convert to ppm monopersulfate, multiply the result obtained by a factor of 5.

$$\text{Monopersulfate Level} = \text{Total Oxidizer} - \text{Total Chlorine}$$

Test strips are also available for analyzing monopersulfate itself. Be sure to check the strip manufacturer's test instructions to determine at what concentration chlorine or bromine will interfere with the monopersulfate test.

## Sidebar: More on monopersulfate

Potassium monopersulfate was developed by the DuPont Company in the mid-1950s as an oxidizer for use in commercial products and processes. It is sold as a raw material to formulators under the trade name Oxone® and is marketed under various brand names as a shock treatment. (Monopersulfate is also used in some "two-part" bromine sanitizing systems to oxidize bromide salts to the active sanitizer hypobromous acid.) Since monopersulfate doesn't contain chlorine, it won't produce chloramines or chlorine odors and will not bleach vinyl liners. Moreover, monopersulfate dissolves quickly at normal pool temperatures without premixing, can be used day or night, and allows swimming to resume after a short waiting period for complete mixing and circulation. It is well suited for indoor use where odors from high doses of chlorine and persistent combined chlorine residuals are magnified.