Interference in Melamine–based Determination of Cyanuric Acid Concentration

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Aqua Clear

Testing for cyanuric acid levels in swimming pools and spas is typically accomplished using a melamine–based turbidity test. Evidence based on experience and experiments shows that there can be a masking, or interference in the melamine–based test, which can cause errors of up to 70%.

A method of correcting the error while testing has been determined, and is described.

Possible directions to pursue in defining the exact nature of the interference are also discussed.

Isocyanuric acid (commonly referred to in the swimming pool/spa industry as cyanuric acid, stabilizer, conditioner, CYA, etc., and referred to simply as cyanuric acid in this paper) is a member of the symmetrical triazine family, and it is used in outdoor swimming pools and spas to protect chlorine against loss from ultraviolet radiation from the sun. Depending on factors such as season and climate, UV–instigated loss of chlorine can be substantial and costly, and consequently the swimming pool industry makes use of cyanuric acid to retard this loss.

The effect of cyanuric acid on the sanitizing capability of chlorine has been investigated and documented. The greatest benefit is, of course, the reduction of chlorine loss due to UV. UV degradation takes as much as four times longer in water containing 35 mg/L cyanuric acid and 1 to 3 mg/L chlorine. However, as the concentration of cyanuric acid increases in water with a constant concentration of chlorine, the ORP decreases and the kill–time increases. Anderson notes that "the addition of 25 mg/L of cyanuric acid at a pH of 7.0 results in a greater decrease in the bactericidal properties of chlorine than an increase in pH of 7.0 to 9.0 in the absence of cyanuric acid" (Anderson 1964). Although pH levels of 9.0 are not common in swimming pools, standard pool pH levels of 7.4 to 8.0 and cyanuric acid levels of 25 to 200 mg/L are common, and are great enough in range for the decrease in biocidal activity to be in evidence.

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Cyanuric acid is generally added to swimming pools/spas via one of two methods: the addition of specific amounts of cyanuric acid powder or granules to the water to achieve a specific desired concentration, or the use of chlorinated isocyanurates, which method controls the chlorine residual but continuously increases the cyanuric acid concentration regardless of the necessity for additional cyanuric acid in the water. Both methods form the desired compounds in the water. "The effect of cyanuric acid is the same at a given concentration whether it is derived from the acid itself or whether it enters the pool with one of the convenient forms of chlorinated isocyanurate disinfectants" (Monsanto 1975 VI–1).

Testing

The swimming pool/spa industry commonly uses a turbidity test to determine approximate cyanuric acid concentrations in water. Essentially, a solution of melamine is added to a volume of water in a special vial. When cyanuric acid is present, an insoluble melamine cyanurate salt is formed. The turbidity of this solution is proportional to the cyanuric acid concentration in the sample. When using the popular Aquality test kit manufactured by Sta–rite, a dipstick with a black dot on the bottom is then lowered into the solution until the dot is obscured by the turbid solution. The dipstick shaft has calibrated markings which, when aligned with the meniscus of the solution yield the approximate cyanuric acid concentration. Monsanto estimates the test precision at 100 mg/L cyanuric acid to be ± 7.5 mg/L (Monsanto 1975 VIII–21). Hach manufactures a DR–100 series colorimeter which also utilizes the melamine turbidity method, but which relies on a 480 nm wavelength beam to determine the turbidity of the solution.

Interference

The author has found that the standard turbidity test for cyanuric acid often registers inaccurately high readings. This was first identified in the course of maintenance of thousands of pools in the Los Angeles Basin over a twenty year span. Similar results have been seen by several other companies in California and Arizona. New pools added to existing service were typically tested, results logged, and treated; as part of the initial treatment, cyanuric acid levels were brought up to 100 mg/L, and the pools were superchlorinated. No cyanuric acid was added to new pools with existing cyanuric acid readings of 100 mg/L or greater. Frequently, it was noted that on many of the pools with initially high cyanuric acid levels, the chlorine residual did not "stabilize", and in some cases it was difficult to establish a chlorine residual. This was not typical behavior in pools containing 100 mg/L of cyanuric acid. Subsequent cyanuric acid tests taken on the problem pools showed that the initially high cyanuric acid levels dropped from 30% to 70%, which would explain the difficulties with the maintenance of the chlorine residual. However, the sudden "loss" of cyanuric acid over a period of 1 to 3 weeks was inconsistent with average losses of cyanuric acid over time.

As mentioned previously, it is commonly accepted that the –s–triazine compounds contribute to the actual cyanuric acid level in the water upon dissolution. However, a consistent pattern was also noted that the pools that exhibited this drop in cyanuric acid readings were pools that had been maintained with trichloro–s–triazine (a chlorinated isocyanurate). The test interference was not noted with pools that had been maintained with sodium hypochlorite or elemental chlorine. Superchlorination seemed to be the consistent solution for correcting the incorrect cyanuric acid readings.

A Solution to the Problem

The author has found that, while performing the cyanuric acid test, a correcting action may be taken to ascertain the "adjusted" concentration. After the addition of the melamine solution to the test sample, and after the precipitate is formed, one drop of $NaOCl^-$ (sodium hypochlorite) is added to the sample solution. The resultant oxidation of the precipitate produces a more accurate reflection of the actual cyanuric acid concentration.

Laboratory Testing

Table 1 contains readings from several pool and spa samples, as well as solutions mixed in the lab. It is provided as a example of waters exhibiting the change and waters exhibiting little or no change. A 1 to 2 mg/L change is not considered significant. Sample sizes were 10 ml, and the tests were conducted with a Hach DR–100 combination colorimeter, model 41100–26. The meter measures free and combined chlorine ranging from 0 to 2 mg/L utilizing the DPD method, pH ranging from 5.5 to 8.0 utilizing the phenol red method, and cyanuric acid ranging from 0 to 50 mg/L utilizing melamine.

Solution	CYA	CYA+$NaOCl^-$	FAC	TAC
Distilled water	0	0	0	0
Distilled water + 0.1g CYA	25	24	0	0
Distilled water + 0.2g trichlor	25	24	(not available)	
Tap water	0	0	0.55	0.65
Tap water + 0.1g CYA	25	23	0.12	0.28
Tap water + 0.2g trichlor	25	19	(not available)	
Apt. Complex pool #1 – trichlor	140	115	1	1.2
Apt. Complex pool #2 – trichlor	90	80	2.6	4.2
Apt. Complex spa – trichlor	55	35	0.3	4.5
Vinyl aboveground pool – trichlor	120	80	1.3	3.6

Table 1 – Testing Results of Various Waters

Source of Interference

Although it is beyond the scope of this paper to conclusively identify the source of the interference, some possible culprits include the following:

- A "residual" species in the cyanuric acid. Cyanuric acid can contain ammelides and ammelines in small amounts. It has been established that both of these chemicals will also precipitate out as melamine salts (Nelson 1975, VIII-10)
- Ammonia
- Chloramine – Samples from swimming pools which exhibited the interference in cyanuric acid testing also contained significant amounts of combined chlorine. Similarities in the composition of chloramine and cyanuric acid could cause chloramine to react with melamine to form a precipitate

It is significant to note that the radical drop in cyanuric acid readings (as opposed to cyanuric acid concentrations) occurs only after superchlorination.

Consequences of Inaccurate Testing

A misdiagnosis of the pool condition, because of an inaccurate test, can lead to costly and unneeded corrective measures. If the level is too low, results can include poor sanitizer control, inadequate disinfection, algal blooms, and other poor water conditions. Correction for this problem is relatively easy – the addition of cyanuric acid until the desired level is achieved. If, however, the level is too high, results can include premature draining, and less effective treatment of the pool water. Correction can be difficult.

There is debate in the industry as to the most effective level of cyanuric acid, with recommendations ranging from as low as 25 mg/L to as high as 150 mg/L (Hamilton 1991, Steininger 1991). However most jurisdictions do impose limits on the allowable concentration of cyanuric acid in swimming pool/spa water. These limits may range as high as 200 mg/L and as low as 100 mg/L. A difficulty with this limit is the lack of an effective means of lowering cyanuric acid concentrations short of draining and refilling all or part of the pool/spa. Nanofiltration and melamine precipitation can both be successful, but neither are cost–effective. In some cases, as in Los Angeles County, the Health Department requires such specialized treatment or draining of the pool water when cyanuric acid concentrations reach 100 mg/L. There are at present no recognized interferences in the common testing method, hence no adjustment is made for possible test errors. Based on empirical evidence, the amount of interference seems to be proportional to the amount of –s–triazine compounds used in the water treatment. Heavily used swimming pools may consume hundreds of pounds of –s–triazine compounds over the course of a year, thereby causing greater test errors. Field inspectors may cite or close pools based upon what appears to be an incorrect assessment of the cyanuric acid concentration.

References

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About the Author

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