Analysis, Measurement and Testing Part II

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This report covers the second part of the talk on testing methods and errors given at the 1998 NSPI Convention held in New Orleans, LA. The first part was given by Tom Seechuk of LaMotte Company while the second part was given by Neil Lowry of Lowry & Associates.

Part 1 – ReplacementReagents

Many firms supplying the pool and spa industry, especially those who manufacture plastic goods such as thermometers, leaf catchers, vacuum heads, etc., also produce sets of replacement reagents. Such reagents are marketed as a standard replacement pack consisting of orthotolidine (OTO) to measure chlorine and phenol red to measure pH. Pool owners buy such products with no appreciation as to the potential for error such "universal" replacement reagents represent.

A simple rule for replacement reagents is that reagents of a specific brand are used for the same branded test kit. In other words, both reagents and test kits must match. Replacement reagents are made at a certain concentration with a specified dosage (number of drops) for a given sample size and for a given set of color swatches imbedded in the block of the test kit. To purchase at random a set of replacement reagents of a brand not specific for your test kit, and have by chance the reagent concentration, the number of drops, water sample size and color swatches match exactly, is of very low probably. Unfortunately most pool owners are unaware of these factors and the use of universal replacement reagent packs continues to produce inaccurate test results!

The answer is to match test reagents for the exact brand and the specific test kit within that brand name. This is the only method of assuring proper pool water test results.

Part 2 – Testing for Total Alkalinity:

Testing for total alkalinity of pool/spa water is normally conducted by the pool dealer or service company rather than the the pool owner. Usually consisting of three reagents in dropper bottles, this titrimetric method produces results within plus or minus 10 ppm, a level of accuracy acceptable for pool water chemical maintenance. Utilizing a burette for titration rather than adding drops from a bottle will, of course, yield a higher though unnecessary level of accuracy.

The first reagent is a chlorine/bromine neutralizer used to lower or eliminate these sanitizers from oxidizing the colored indicator used in this test. An indicator is the second solution used for end point determination. This reagent, usually a duo indicator consisting of bromcresol green and methyl red, gives a strong contrasting end point color change from green to red, the latter being complementary colors. The red color of the methyl red indicates a pH below 5 in which all the bicarbonate alkalinity has been removed as carbon dioxide. The third and last reagent is the titrant, a weak concentration of an acid such as sulfuric acid, added a drop at a time until the test sample changes from green to red. The drops of titrant employed are then counted and multiplied by the equivalence factor to find the total alkalinity of the sample. For example, many kits use an equivalence of one drop equaling 10 ppm of total alkalinity, so if 12 drops are required to turn the test solution from green to red, the alkalinity of the pool is 120 ppm.

Total Alkalinity Testing Errors: The errors which confuse those testing for alkalinity are really not errors, but rather seeing a different end point than that expected. In the duo indicator the methyl red indicator is quite prone to destruction by high levels of chlorine/bromine. Normally the neutralizer reagent

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will handle chlorine or bromine levels, but high levels of these sanitizers, if not neutralized, will bleach out the methyl red. Destroying the methyl red causes the titration to have an end point from blue to yellow, a significantly reduced color contrasting end point. Ironically this change from blue to yellow is the bromcresol green indicator alone and, while more difficult to observe, will yield proper total alkalinity results! Increasing the amount of neutralizer added will avoid this problem with little effect on the total alkalinity reading.

Part 3 – Testing for Calcium Hardness:

Calcium hardness, not total hardness (i.e., calcium + magnesium) is the measurement required in water balance considerations. Standard calcium hardness titration tests have three reagents. The first is a solution of sodium hydroxide, which, when added, raises the pH to 12 to precipitate the more insoluble magnesium hydroxide so the magnesium hardness will not titrate in the final result. The second reagent is the indicator Eriochrome Black which complexes with calcium ions to yield a carmine red coloration which changes to a pure blue end point. The titrant is a common complexing agent for metals, EDTA (ethylene-diaminetetraacetic acid). The drops of this third reagent are counted and multiplied by the equivalence factor to find the calcium hardness of the sample water. For example, many kits use an equivalence of one drop equaling 10 ppm of calcium hardness; so if 21 drops of EDTA are required to turn the test solution from red to blue, the calcium hardness of the sample water is 210 ppm.

Calcium Hardness Testing Errors: The error in testing for calcium hardness is an interference caused by dissolved copper or iron in the pool water. Pools with steel fittings or filters and copper piping or heat exchangers in contact with corrosive pool water will pull copper and iron into solution. In this case the tester obtains a fading end point. Here the indicator turns from red to a red-purplish coloration with no clear blue end point. The tester keeps adding titrant and after a while loses patience and writes down a number of drops (usually much higher than the true level). The correction of the problem, if iron or copper is thought to be present, is to add two drops of EDTA before commencing with the test. Follow the test through and add back the two initial drops of EDTA to the titrant count. This sum is the calcium hardness. For example, if after adding 2 drops, the test required 26 drops of titrant to reach the blue end point the number of titrant drops for the test would be 28 (26+2).

Part 4 – Testing for Cyanuric Acid:

An analytic bulletin from FMC, the initial producers of cyanuric acid (CYA), showed that at a slightly acidic pH the compound melamine will form a type of melamine–cyanuric acid complex which will precipitate from solution. The initial test procedure outlined a gravimetric method for CYA where this precipitate was filtered and weighed. Today field tests are based on turbidity measurements. Here the tester lifts a "dip stick" which has a black dot protruding from the bottom of the stick until the black spot becomes visible. The concentration of the CYA is designated by the readings on the side of the stick. In other CYA turbidity measurements, a tube containing a black dot on the bottom is filled with the white turbid solution until it disappears and reading are taken from the markings on the outside of the tube.

Cyanuric Acid Testing Errors: The measurement of when a "black dot" appears or disappears is tenuous at best. Errors in CYA readings are large relative to those of say, total alkalinity. It is fortunate that the level of cyanuric acid in pool water is not so critical as to demand accurate determinations. In spite of the low test requirement, there remain errors with this test that can compromise CYA's rough determination. The first error has to do with the fact that the melamine–CYA complex has a solubility dependence with temperature. The higher the temperature of the testing solution, the greater the solubility of the melamine–CYA, the less the turbidity and the lower the reading. Some dealers put the melamine reagent in a refrigerator to cool so that mixing with a pool water sample brought into their store avoids elevated temperatures of the test water. A warning about this method! At cool temperatures, over time, melamine may crystallize out of solution in the reagent bottle and one will always find false low or non–existent levels of cyanuric acid in the pool water test samples. Turn the bottle upside down to see if crystals have formed. If so, let the reagent warm to room temperature and allow the crystallized melamine to redissolve.

The second and last error occurs when the CYA concentrations are in the higher range of 60 ppm plus. Because the marking on the stick or tube are logarithmic, the spacings of the levels are "squashed" together at high readings, vastly increasing relative error of measurement. This is the nature of the test and nothing can be done to alleviate this problem except diluting the sample and then multiplying the results by the reverse of the dilution factor. This latter process, however, has its own inherent errors.

Often many pool professionals will attempt to solve a water chemistry problem with little success due to the fact that they are chasing a false test kit reading. Prevalent thinking assumes that the test kit results are always correct and that the problem lies in the pool water. Hopefully this seminar Part I and Part II will cause such professionals to realize that there are limitations and errors in testing methods. Making sure that a problem discovered lies with the pool water and not with false water test results is the purpose of this talk.

About the Author

R. Neil Lowry, Ph.D. is a graduate of the University of Western Ontario in Honors Chemistry and received his Doctorate in Inorganic Chemistry from Cornell University. In the pool industry since 1977, Dr. Lowry has his own consulting firm, Lowry & Associates, and is the exclusive Canadian distributor for Taylor Technologies. Dr. Lowry has published extensively in industry trade journals and been a regular speaker at various pool water chemistry events. He is also a member of the NSPI's Chemical Treatment and Process Committee and has given several talks at past NSPI trade shows. Dr. Lowry is a consultant to governments and numerous corporations in the areas of label registration, chemical formulations, marketing and text writing. He was contracted by Agriculture Canada to standardize all pool chemical labels falling under the Pest Control Products Act of Canada. More recently Dr. Lowry created Spa Water Standards for commercial spas under the jurisdiction of the Ontario Department of Health.