

A Review of Methods for Testing of Cyanuric Acid Residuals in Swimming Pool Water

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Many states regulate the quantity of cyanuric acid that may be present in swimming pool water. Operators of commercial facilities must monitor the cyanuric acid level and maintain it within the state requirements. These state requirements may range from a maximum of 40 ppm to as high as 200 ppm. Current testing methods include turbidity-based testing and indicator-color-change based testing. These methods vary greatly in their accuracy and precision. A review of these methods and their testing ranges, accuracy and precision ranges as well as test interference reveals situations which create problems for commercial pool operators and public health officials. Laboratory testing methods available for use by pool dealerships provide some improvements over poolside testing methods, but also have deficiencies in range, accuracy and precision. Data from all types of testing were collected on a group of samples and are presented. These data illustrate some of the issues currently needing addressing with improved testing methods.

Cyanuric Acid Residuals

Various methods are available for determination of the residual of cyanuric acid in water. These methods do not meet the current needs of commercial pool operators and the swimming pool industry. Public health inspectors, commercial pool operators as well

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as pool service technicians and retail store personnel need accurate and precise methods for measuring cyanuric acid residuals.

Public health inspectors and pool service technicians need methods that are easily transportable and do not require A/C current for operation, while a commercial pool operator needs a method that is simple, does not require dilutions and would not be severely compromised by being in a high humidity environment. Another consideration of a test method is the range of accuracy, the increments across that range as well as the knowledge that interference may have occurred. For example, residuals as high as 200 ppm are acceptable in some states; therefore the test method should provide a range at least to 200 ppm, but preferably to 250 ppm. Across the test range, the increments must be small enough to provide the tester with information to make valid decisions. For cyanuric acid residuals, in the lower ranges (essentially below 125 ppm) incremental changes should be set for 10 ppm. Above 125 ppm, the increments at 30 ppm would be adequate for most situations.

Of potentially even more importance is the ability of the tester to know if interference has occurred in a test, creating a possibility for error. Several possible interference are recognized in the current test methods. However, these are not widely known by the users of the methods and the methods themselves have no indicator to the tester that interference has occurred. The result is often wide variance in test results on the same sample.

Two basis methodologies are employed for determination of cyanuric acid residuals in swimming pools when testing is done poolside. One method is based on the formation of an insoluble precipitate with melamine and cyanuric acid. The other method is based on a color change in a reagent that is pH sensitive.

Turbidimetric Basis

The turbidimetric basis uses a melamine reagent that may be used as either a tablet or a liquid. The sample of water is mixed with the reagent. The more turbid the resulting solution, the higher the concentration of cyanuric acid present in the sample.

The degree of turbidity may be determined by visual means or by instrumental analysis. One test kit provides a chamber in which to create the mixed solution along with a stick that is curved at the bottom to create a flat surface, on which is located a black dot. Once the sample has been mixed with the reagent, the stick is raised and lowered within the solution. The tester locates the stick at the shallowest point in the chamber that makes the tester unable to see the black dot. Holding the stick steady at this depth, the tester then observes the chamber from the side. A marking on the chamber is then matched against the markings on the stick and a corresponding concentration of cyanuric acid in the sample is determined. A variation on this method uses a tube-within-a-tube design for the test chamber.

Other kits use a mixing vial to mix the sample and reagent. The mixture is slowly dispensed into a chamber that has a black dot at the bottom. The tester stops adding the solution as soon as the black dot has been obscured from sight by the turbid solution. The height of the solution in the chamber is compared to markings on the

chamber to determine a corresponding cyanuric acid concentration.

A spectrophotometer or a turbidimeter may be used to measure the degree of turbidity the sample solution. The degree of turbidity is then converted to a concentration of cyanuric acid present in the sample.

The various kits using a visual determination have ranges from 0 ppm to 100 ppm and from 0 ppm to 200 ppm and employ both tablet and liquid reagents. The instrumental methods use a liquid reagent and provide results for ranges of 0 ppm to 50 ppm and 0 ppm to 80 ppm.

In all turbidimetric methods the increments vary across the ranges. As each system approaches the maximum of its range, the increments grow larger. In several instances it is difficult to distinguish between residuals above 70 ppm. Note the markings on the stick in Figure 2.

Colorimetric Basis

The colorimetric method depends upon the color change of a reagent that is affected by the pH of a solution. A colorimetric method using liquid reagents is covered by a patent (U.S. Patent Number 4,855,239, Issued on August 8, 1989 to Chauncey O. Rupe), but has not been commercialized by the Assignee, Environmental Test Systems, Inc. This method uses an aqueous solution of a stabilizer, monoethanolamine and a thymolsulfonephthalein compound. It is believed that interference problems related to "normal" pool water may have made commercialization difficult.

A colorimetric method employed with test strips uses melamine and a pH-indicating reagent. The solution is impregnated into the pad on the strip and the color of the pad is compared to a set of color standards, representing various concentrations of cyanuric acid. The test strip may also be read by an optical scanner and a concentration of cyanuric acid determined by comparison to known standards. The output from the instrument is generally fed to a computer for reporting of the concentration of cyanuric acid.

The test strips have a range of 0 ppm to 150 ppm, with standards for visual comparison at 0 ppm, 50 ppm, 100 ppm, and 150 ppm. When read by the scanner, the strips provide results from 0 ppm to 100 ppm, with increments increasing at the upper end of the range.

Interference in Turbidimetric Tests

All turbidimetric test methods are sus-

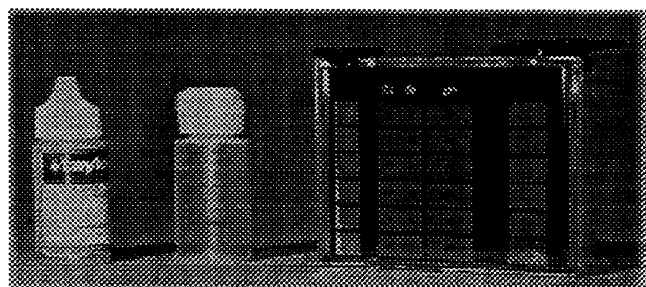


Figure 1 – Turbidimetric Test using view tube

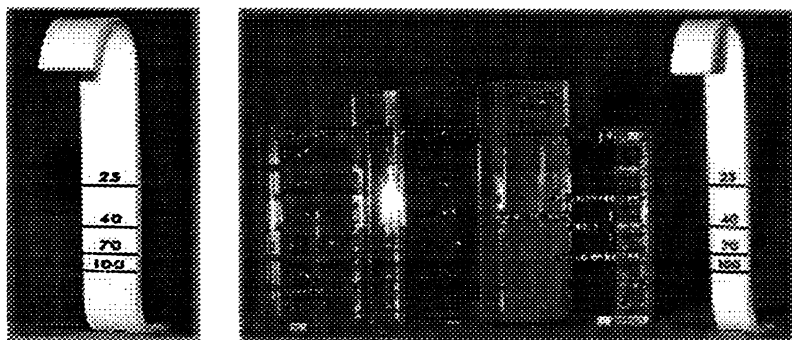


Figure 2 – Turbidimetric Test using measurement stick

ceptible to interference due to water sample temperature and excess chlorine residuals. If the temperature of the water at the time the tablet is added to begin the test exceeds 77°F, a falsely low reading could occur. With the liquid reagent test, refrigeration of the reagent is recommended. For accurate test results, the temperature of the water sample and reagent mixture should not exceed 70°F. If the sample temperature is over 70°F, a falsely low reading could result.

When chlorine residuals in the sample water exceed 5 ppm, the solubility of the melamine-cyanuric acid complex is affected. The competition for the cyanuric acid by the chlorine present creates a lower quantity of the melamine-cyanuric acid precipitate. The result is a lower turbidity of the sample, and a falsely low result.

Frequently testers are not aware of these sources of interference. Additionally, many testers do not determine the temperature of the water prior to beginning the test.

Turbidimetric Testing Method Effects

In addition to errors in results that are caused by interference, there are also test methods that are important to obtaining the correct residual. Improper timing of the test is one of the most common method errors. In order for the full formation of all the melamine-cyanuric acid precipitate to occur, the sample must be mixed with the reagent, then allowed two minutes of reaction time. Only after this two minutes can an accurate result be obtained. This reaction time is required for both the liquid and tablet reagents and will affect the test results for both visual and instrumental readings.

A dirty viewing tube or a measuring stick that has been allowed to accumulate the precipitate from previous tests onto its surface will also cause falsely low results. The concept of cleaning testing apparatus is often foreign to the individuals involved in the testing process. Service Industry News provides excellent information on their website concerning testing, but even this source does not mention the need to keep the testing equipment clean. For instrumental readings, an inadequately cleaned cuvet or sample cell will also cause inaccurate results.

A third source of inaccurate results for the visually read tests is performing the test in inadequate lighting. Because the basis of this test is the ability to see a black dot through a turbid solution, any situation that would affect an individual's visual acuity would affect the results of the test. These tests are designed to be conducted in the lighting typical of a poolside situation or in a brightly-lit laboratory or store. If the test were conducted in a poorly lit area, the results would be reported as higher than the ac-

tual concentration that was present.

Colorimetric Test Interference

The colorimetric test is also vulnerable to certain interference. As with the turbidimetric tests, a chlorine residual in excess of 5 ppm can affect the results. However, the effect is not significant for this test method until the chlorine residual is approximately 10 ppm.

Because the colorimetric test is based upon changes in reagent relative to pH, both pH range and total alkalinity range have an effect on the test results. Accurate results can be obtained in the pH range of 7.2 to 7.8. Total alkalinity outside the range of 80 ppm to 120 ppm will cause inaccurate results.

Colorimetric Test Method Effects

Test strip results are not vulnerable to as many errors as are the turbidimetric tests, but there are some considerations for obtaining the most accurate results. Test strips are vulnerable to moisture, as the reactions of the reagents will begin once the pad has become sufficiently moist. Strips may be exposed to moisture if the container is not properly closed following removal of a strip. Many testers are also not cautious enough with drying of their hands prior to reaching into the container to obtain a strip.

As simple as the instructions for use of test strips may seem, the dip and read instructions are sometimes not properly executed. Some strips require a swishing of the strip within the sample of water for a specified period of time, while others are simply to be dipped and removed. Some strips are to be held horizontal, causing the water to puddle on the pads, while others are to be shaken gently to remove excess water or blotted in a prescribed manner. Some strips are to be read immediately, while some require a short waiting time or a particular sequence of reading the various pads on the strip, resulting in a "built-in" waiting time. It is important that the testers read and follow the instructions for the particular strip that is being used.

Test Results Vary

Having examined some of the factors that can influence the accuracy of various tests, let's take a look at some data using these methods. Figures 3 and 4 present data collected in 1998 using four of the methods described above. The same tester performed all tests, but samples were prepared as blind samples. The samples used were pool water samples collected from various sources with a range of all the various water balance parameters and chlorine residuals. The

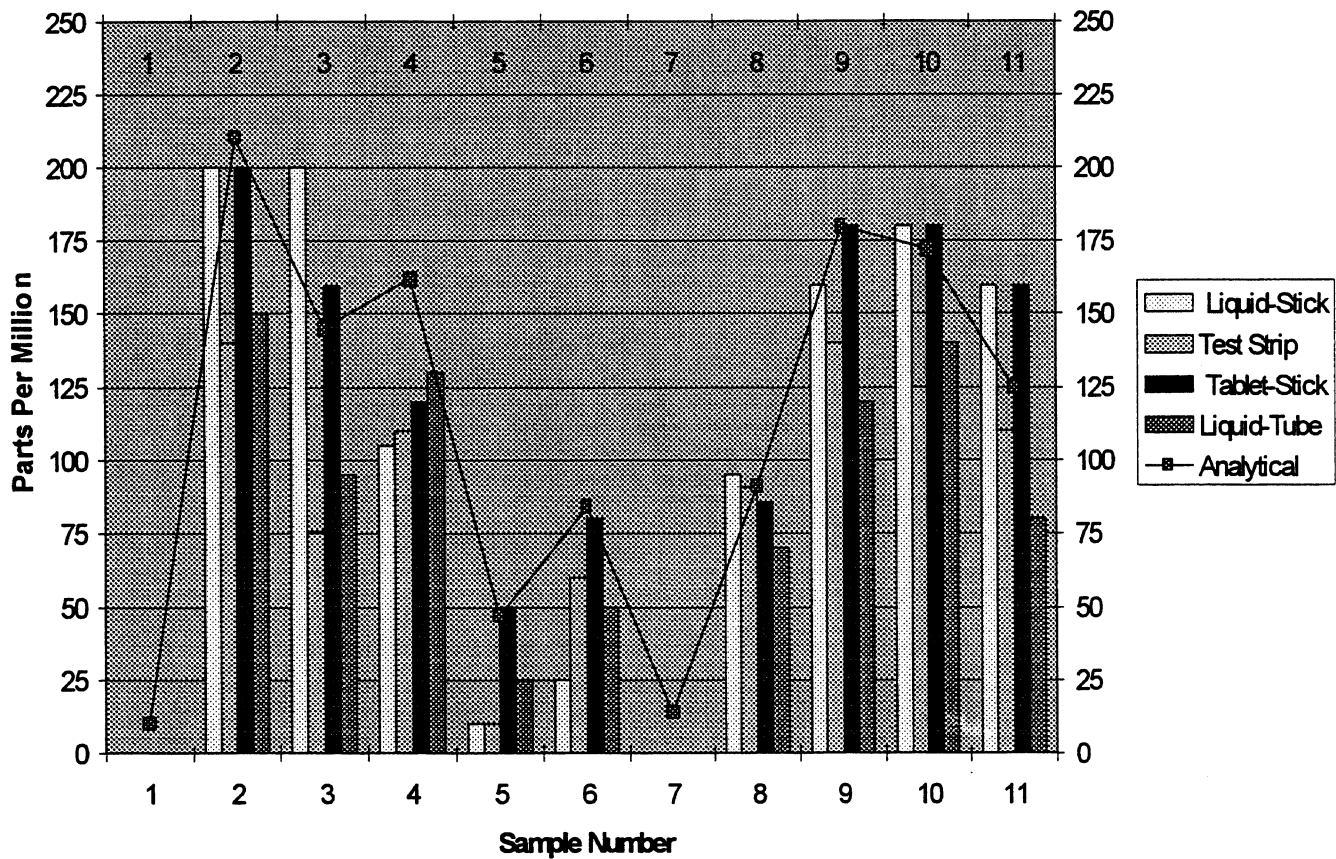


Figure 3 – Cyanuric Acid residuals on random water samples – 1998 data

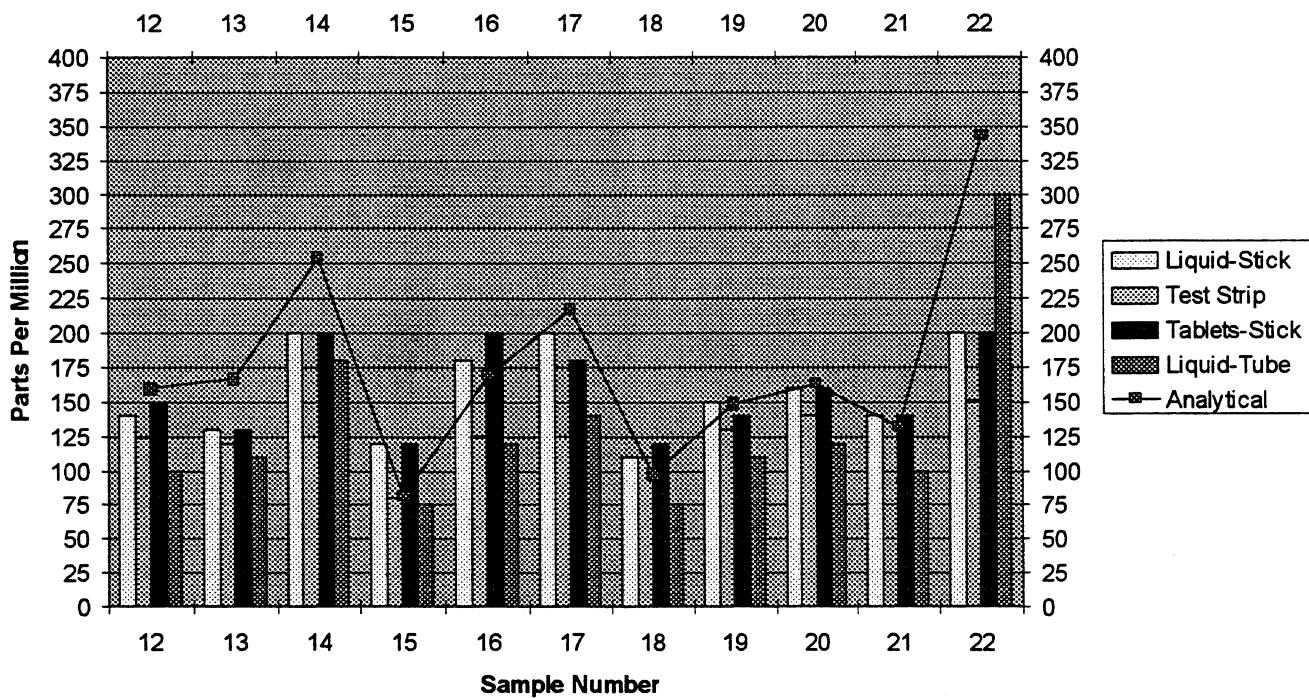


Figure 4 – Cyanuric Acid residuals on random water samples – 1998 data

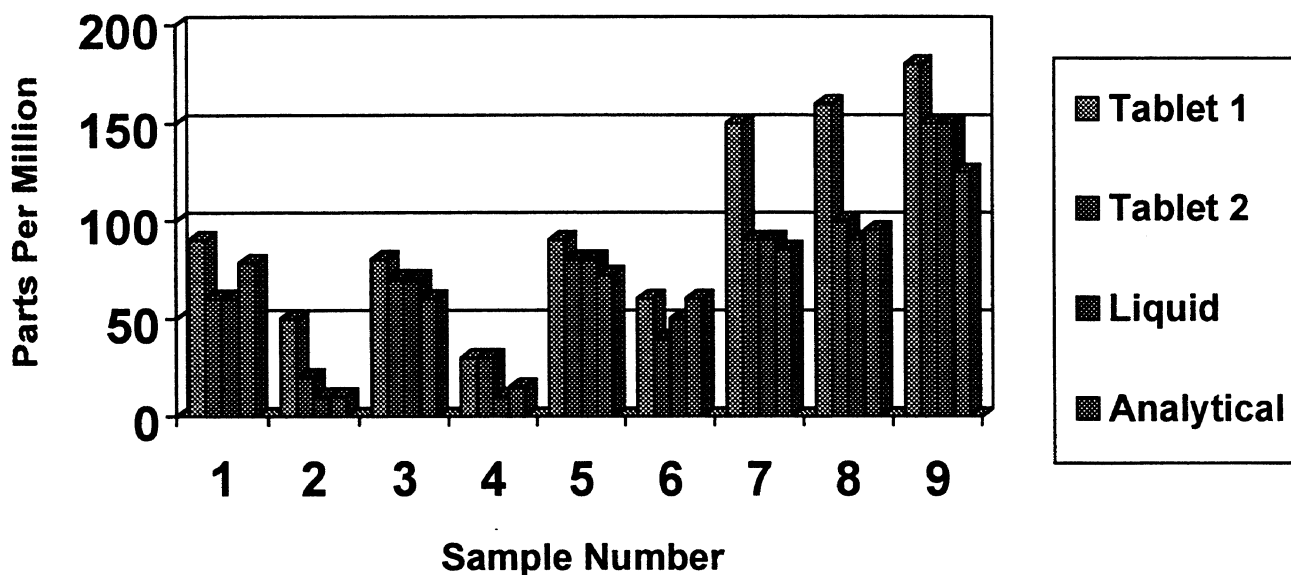


Figure 5 – Cyanuric Acid residuals on random water samples – 1992 data

chlorine residuals ranged as high as 43 ppm and pH ranged as low as 2.9. The analytical method reported here is based on HPLC analysis using a method developed in the Analytical Laboratory at BioLab, Inc.

Figure 5 provides information on data from samples tested in 1992, again with a variety of methods. Test strips were not used for this data collection and the analytical method used was the gravimetric method found in Standard Methods.

For the 22 samples tested in 1998, there was one trend for the data in that the analytical test results tended to provide a higher value. For the 1992 data, the trend was a lower reading produced by the liquid reagent based test than for other methods. However, note that these are trends and for any one sample, this trend may prove false.

Where are we today?

Reflecting on this information leads one to ask about the impact of the variations in test results, the potential for interference and method errors that occur and the adequacy of the current tests for the pool market. These factors create situations for Commercial Pool Operators and Public Health Officials where the proper course of action is simply impossible to determine. If a pool operator has tested the cyanuric acid residual and found it to be in the acceptable range, but the Public Health Inspector finds it to be too high, the pool may have to shut down and drain a

portion of the water to dilute the cyanuric acid into an acceptable range. The pool operator was following the proper procedures, but the outcome is a pool that will not be available for swimmers and will incur added costs for the replacement water. This situation causes negative feelings between the pool operator and the Public Health Inspector, two earnest individuals each believing they are doing their job correctly. Additionally, the environmental impact is not a positive one as water that may well be acceptable for swimming has been sent into a storm or sanitary sewer, and additional potable water removed from the supply to refill to pool. Yet another point for consideration is the impact that occurs when a Public Health Department is writing regulations. In determining what cyanuric acid residual will be acceptable as the upper limit, the limitations of the test kits would potentially lead to a choice of 100 ppm, while data exists to support that 200 ppm is a very realistic limit.

A concerted effort on the part of test kit manufacturers to overcome these limitations is needed. In directing this effort, the following needs of the testers should be incorporated:

- Ability to measure cyanuric acid residuals up to 250 ppm
- Increments of 10 ppm up to 100 ppm
- Increments of 30 ppm above 100 ppm
- Ability to know when an interference has occurred.

About the Author

Mary Costanzo received her BSA degree with a major in biochemistry from the University of Georgia. She joined Hydrotech 1988 and worked as a Technical Services Manager. In 1991, when BioLab and Hydrotech joined, Mary became Manager of Technical Services for BioLab. She is involved in seminar presentations, product claim substantiation studies, field trials for new products, competitive product analysis, and the Water Analysis Laboratory. She also directs the Quality Assurance Laboratory.

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