

PERACETIC ACID

TWO TESTING METHODS: COMPARISONS AND DISCUSSIONS

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INTRODUCTION:

Peracetic acid (PAA) is available from several manufacturers in the United States. Its use as a sanitizer and disinfectant is growing in the food, beverage, wine, dairy, and water treatment industries as a more effective and environmentally friendly replacement for chlorine and other sanitizers. There are also numerous test procedures and methods of analysis for these PAA products, and this laboratory examination will evaluate the over-all reliability and accuracy of two such test procedures. One test procedure evaluated herein is manufactured and distributed commercially by the LaMotte Company. It is called "Peracetic Acid Test Kit" #7191-01. The other is Enviro Tech Chemicals, Inc. "Test Procedure #103" for Perasan 'A'.

Some concerns have been raised about the accuracy and reliability of test kits and their associated results. The end user must have some confidence in the testing kit they are using due to the fact that minimum levels of sanitizer must be maintained in order to have confidence the anticipated sanitation or disinfection results are accomplished. In addition, erroneous or unreliable test results may dictate the feed rates and increase the resultant costs associated with the use of the PAA solutions, which could result in less reliable efficacy and higher use costs than would otherwise occur. Therefore, accurate and reliable testing methods are important to control costs and assure reliable food or beverage product integrity.

OBJECTIVES:

This laboratory evaluation will compare the accuracy and reliability (precision and repeatability) of two test kit methods that are designed to analyze for peracetic acid in a water matrix.

Both test kit methods will be evaluated at two temperature regimes and at 3 concentrations of a known amount of peracetic acid, i.e. 70 ppm, 140 ppm, and 210 ppm. The temperature regimes are 66° F and 100° F.

In addition to ambient or room temperature sanitizer concentration testing, peracetic acid products are often used at elevated temperatures for reasons of increased efficacy and the need for decreased exposure times. On-site sampling for in-house testing is often obtained at these higher temperatures, and drop-kit testing is done on the resultant samples (at higher temperatures than usual). Therefore, this evaluation will incorporate the temperature variability to determine if these testing methods are influenced by these conditions, and if so, by what degree.

MATERIALS AND METHODS:

Potable drinking water (tap water) was chosen as the testing diluent for preparing the end-use PAA concentration standards. Modesto, CA city tap water has a pH of 7.8 and contains 150 ppm of hardness (average). This water would simulate a much better real-life condition-of-use than distilled or deionized water, and it was used throughout the present evaluation unless otherwise noted.

In November 2003 Enviro Tech obtained a new LaMotte Company "Peracetic Acid Test Kit" #7191-01. It is a dual-purpose kit that has the ability to test for peracetic acid and hydrogen peroxide independently. Only the peracetic acid portion of the test kit procedure will be used for the purposes of this evaluation. The kit consists of a sample vial, sulfuric acid, ferroin indicator, potassium iodide developer, and sodium thiosulfate as the titrant. 10 mls of the test solution is added to the vial, then 10 drops of sulfuric acid, 1 drop of ferroin, 1 drop of potassium iodide, and then titrated to an orange-pink end point using sodium thiosulfate. Swirling is required after each step. Each drop is equal to 15 ppm active PAA, according to the directions.

The Enviro Tech test method uses 5 solutions. 5 drops each of solution #1-4 are added sequentially to a 5 ml. sample, and the dropper test solution #6 is used as the final titrant. Solution #1 is potassium iodide, solution #2 is phosphoric acid, solution #3 is ammonium paramolybdate, solution #4 is a starch indicator, and solution #6 is sodium thiosulfate. The end-point (as described in the directions) is water-clear (for 15 seconds), and each drop is equal to 5 ppm.

Using deionized laboratory-grade water, a 10,000 ppm stock solution was prepared from a freshly analyzed PAA material derived from a 5.6% active PAA formulation known as Perasan 'A'. The appropriate amount of the Perasan 'A' solution was weighed into 500 ml flasks, to each was added Modesto City tap water. The amount of added water was sufficient to obtain a final concentration of active PAA of 70, 140 and 210 ppm. In the case of the elevated water temperature test, the diluent water was heated to 112° F and then added to one flask containing the pre-weighed amount of PAA necessary for the respective concentration. The warmed solution was subsequently analyzed by two technicians simultaneously, each using one of the aforementioned test kits. The average temperature reading during the 5 replicate testing was 100° F, which is reported in Table 2 and Chart 3. The room temperature analysis and results are reported in Table 1 and Chart 1 & 2.

RESULTS AND DISCUSSIONS:

Both test kits evaluated in this report consistently under-reported the actual concentration of PAA present in the test solutions. Considering both test kits used sodium thiosulfate as the titrant and that each drop of the ET solution equaled 5 ppm, and each drop of LaMotte's solution was 15 ppm, it was postulated that as the concentration of the known standard increased the accuracy (precision) of each concentration series would also increase, especially the LaMotte test procedure. Such was the case with the ET test procedure, at both temperature regimes, but not for the LaMotte method.

At room temperature the accuracy of the LaMotte kit actually decreased from -14.3% at 70 ppm to -24.3% at the 210 ppm concentrations. At the same time the ET kit increased in accuracy from -5.7% at 70 ppm to -0.9% at 210 ppm, which would be expected, considering more drops at higher concentrations would improve precision. The average accuracy of each method at all concentrations at 66° F was -2.9% for the ET test kit, and -18.3% for the LaMotte kit. This 6.3 fold difference is significant, in that one would expect only a 3-fold difference, considering the inherent difference in drop strength, i.e. 5 ppm vs. 15 ppm. Most curious, however, is the fact that as the concentration of the test solutions increase above the 140 ppm level, the precision of the LaMotte test kit *decreased* significantly, which is the opposite of what one would expect. The errors are consistently on the low side of actual concentrations.

At the elevated temperature regimes the accuracy of the ET method increased when compared to the room temperature analysis. The average deviation percentage for all 3 concentration ranges at the elevated temperatures dropped to -0.8% (vs. -2.9% at room temperature). Indeed, the LaMotte kit fared much better at the 70 ppm concentration at elevated temperatures. The LaMotte test kit average deviation dropped from -14.3% at 66° F to -5.7% at 100° F, which equaled the ET procedure (percent deviation) at room temperature and at 70 ppm.

At the 140 ppm concentration and at elevated temperatures the LaMotte kit failed to yield a stable end point. An orange-pink color that is stable for 15-20 seconds is the described end point, but at elevated temperatures this color faded very quickly. When more thiosulfate titrant was added the end point faded at an accelerated rate. After adding more than twice the amount of drops that should have been necessary, the test was suspended as being impractical. The same difficulties were experienced using the 210 ppm concentration at the higher temperature regime, and this test was also terminated. Subsequently, the lab technician allowed the solutions to cool gradually and performed frequent titrations to determine at which temperature the test kit could be used to obtain reliable readings. It was determined that sample temperatures below 75° F (24° C) were necessary to obtain reasonably reliable and stable end-points using the LaMotte method.

It should be noted here that both kits were tested against a blank water sample at 0 ppm of peracetic acid. Both kits did not register positive for PAA. However, since the LaMotte kit is a 2 part-kit for hydrogen peroxide and PAA, we ran a hydrogen peroxide analysis on the tap water blank. The results were an apparent 50-100 ppm of hydrogen peroxide in the tap water.

The directions indicate each drop of peroxide titrant is equal to 50 ppm hydrogen peroxide. Therefore, one must be very careful not to consider or interpret low levels of either analyte (PAA or H₂O₂) using the LaMotte test kit.

Although both test kits use sodium thiosulfate as the titrant, the methods used to obtain the PAA concentration are quite different. The oxidative activity of hydrogen peroxide at lower concentrations is much lower than peracetic acid. The theory of the potassium iodide-sodium thiosulfate test kit is potassium iodide (KI) is added to the sample and is converted to iodine (I₂) by the oxidative action of the PAA (oxidant) with the iodide ion. The amount of iodine that is formed is proportional to the concentration of the oxidant. It becomes simple math to multiply the number of drops times the ppm equivalent per drop of solution. However, hydrogen peroxide can also oxidize iodide to iodine, especially if present in sufficiently high concentrations, or at elevated temperatures. Increasing a solution's temperature is universally accepted as a way to increase the activity and/or efficacy of most chemicals, including such products as PAA or hydrogen peroxide. This would help explain why the LaMotte kit becomes less accurate for PAA as the concentration and temperature increases, which becomes visually evident in both Table 1 and 2, and Chart 2 and 3. There is a phenomenon at work called "hydrogen peroxide bleed". As the temperature of the solution increases above 75° F and/or the total hydrogen peroxide concentration increases, with a proportional PAA increase, the 'bleed' effect of the hydrogen peroxide becomes more pronounced, and increasingly oxidizes more of the iodide to iodine, giving the same appearance and effect as the peracetic acid. This will have variable effects on the test kit's orange-pink end point, and the operator-technician is forced to subjectively guess where the end-point emerges or terminates. This leads to large operator margins of error, i.e. trying to distinguish the end point, which is quite transient.

The ET procedure, although it also uses potassium iodide and sodium thiosulfate, utilizes a different chemistry approach to eliminate the hydrogen peroxide “bleed” phenomenon. The solution #3 in ET’s procedure is ammonium paramolybdate. Adding this compound converts all the active oxygen species capable of oxidizing the potassium iodide to iodine. The #4 solution is starch, which forms a deep blue starch-iodine complex that disappears at the end point. This water-clear end point is very distinguishable by the untrained technician. The number of drops of sodium thiosulfate added releases all the active oxygen species, thus eliminating the hydrogen peroxide ‘bleed’ effect. This procedure/method is highly accurate and precise, as can be seen in the Tables and Charts listed on the following pages. The method eliminates potential ‘bleeding’ effects of hydrogen peroxide, and also minimizes interferences caused by water hardness and elevated solution temperatures.

However, the down-side trade off is that the ET Perasan ‘A’ test kit is not a commercialized product for all PAA formulations, and the test method used is specific to Enviro Tech’s Perasan ‘A’ product. Some formulated peracetic acid products have different PAA to hydrogen peroxide ratios, and thus the ppm per drop of titrant values may be different when testing alternate formulations from other suppliers. The Perasan ‘A’ formulation is a minimum 5.6% peracetic acid and 26.5% hydrogen peroxide, which equals a 4.7:1 peroxide to PAA ratio.

One could, however, use the ET test kit for alternate formulations by using a correction factor. For example, FMC’s Vigorox is 5.1% PAA and 21.7% hydrogen peroxide, which equals a 4.2:1 peroxide to PAA ratio. One would simply multiply the number of drops used with ET’s test kit by 5.25 (rather than 5.0) to yield actual active PAA. Ecolab’s Oxonia Active is nearly identical to Enviro Tech’s Perasan ‘A’ product, so no conversions would be necessary.

Enviro Tech’s Procedure #103 is not available to the general public, but is available to commercial and industrial end-users directly through Enviro Tech or one of its authorized distributors.

CONCLUSIONS:

- At 66° F the measurements using both the Enviro Tech and LaMotte test kits correlate linearly with the actual PAA dose.
- The percent accuracy of measured vs. actual dose at 66° F is far higher for the Enviro Tech test kit method vs. the LaMotte method. The accuracy of the LaMotte kit actually decreased from -14.3% at 70 ppm to -24.3% at the 210 ppm concentrations. At the same time the ET kit increased in accuracy from -5.7% at 70 ppm to -0.9% at 210 ppm.
- At elevated temperatures the measurements using the LaMotte kit failed due to the rapid bleed-through of the hydrogen peroxide component, making observation of the true end point impossible.
- At elevated temperatures the Enviro Tech test method actually increased its accuracy vs. the 66° F measurement. The *average deviation percentage* for all 3 concentration ranges dropped to -0.8% (vs. -2.9% at room temperature).

RAW DATA

TABLE 1

PAA Actual vs. Measured ppm @ **66° F**

70 ppm 140 ppm 210 ppm

ET Test	LaMotte	ET Test	LaMotte	ET Test	LaMotte
70	60	140	120	205	135
60	60	135	120	210	165
65	60	135	120	215	165
65	60	140	105	205	180
70	60	135	120	205	150

Average Result	66	60	137	117	208	159
Deviation % from Actual	-5.7%	-14.3%	-2.1%	-16.4%	-0.9%	-24.3%
Standard Deviation ppm	3.77	0	2.73	6.71	4.75	17.1

Enviro Tech Test Kit Correlation Coefficient (R²) = 1.0

LaMotte Test Kit Correlation Coefficient (R²) = 0.9924

TABLE 2

PAA Actual vs. Measured ppm @ **100° F**

70 ppm 140 ppm 210 ppm

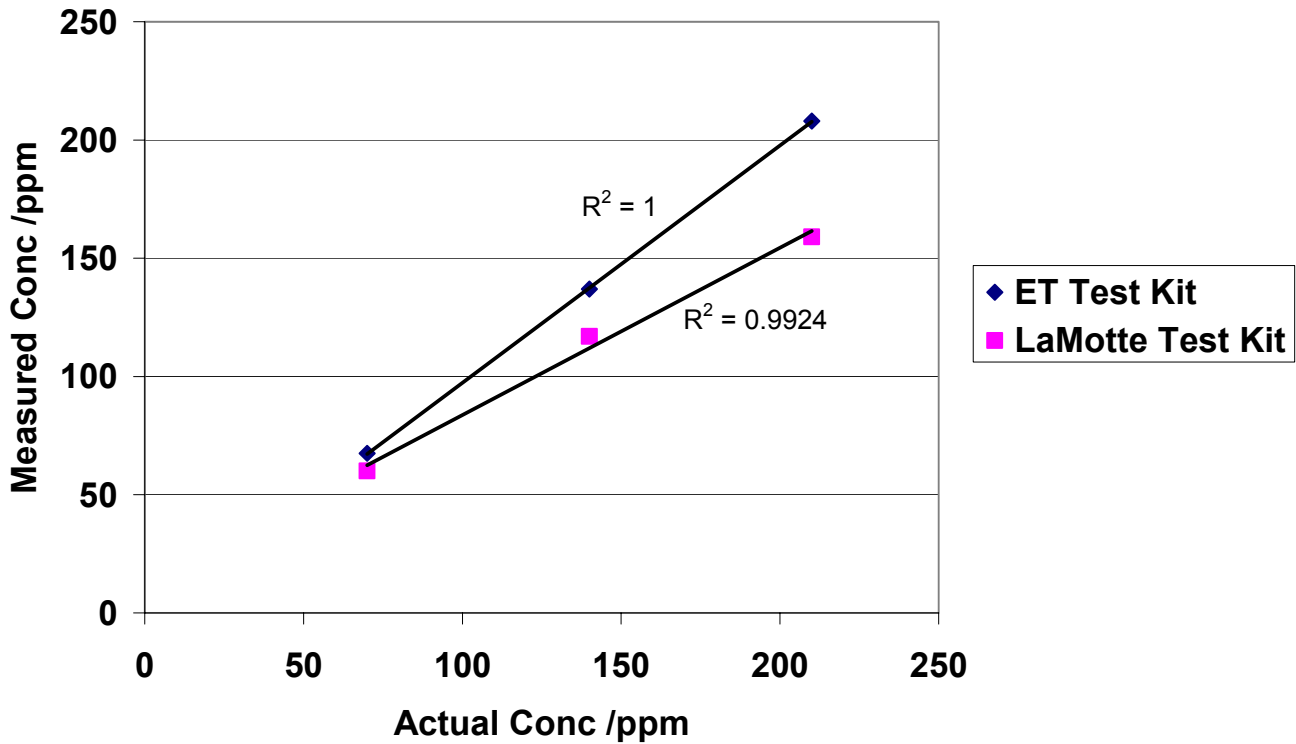
ET Test	LaMotte	ET Test	LaMotte	ET Test	LaMotte
65	60	135	nr	205	nr
75	75	140	nr	210	nr
75	60	140	nr	210	nr
65	75	140	nr	205	nr
70	60	135	nr	210	nr

nr = not readable (end-point was not stable)

Average Result	70	66	138	0	208	0
Deviation % from Actual	0.0%	-5.7%	-1.4%	100%	-0.9%	100%

CHART 1
Standard Deviation Correlation Coefficients

Measured vs. Actual PAA Concentrations



The above Standard Deviation Correlation Coefficient Chart is **only** for 66° F. (100° F no data)
Data derived from Table 1.

CHART 2

**% Accuracy of Measured vs. Actual PAA Dose
Temperature 66 deg. F**

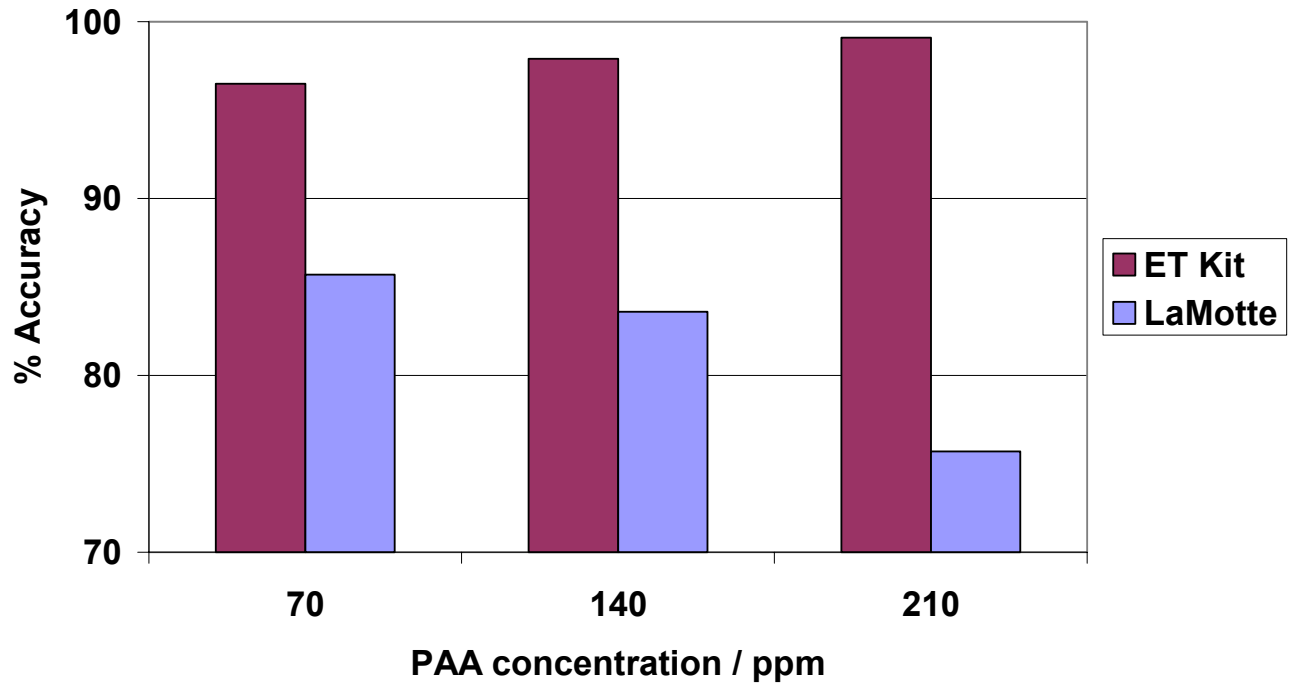


CHART 3

**% Accuracy of Measured vs. Actual PAA Dose
Temperature 100 deg. F**

