Evaluation of the Palintest Kemio on the Quantification of the Peracetic Acid

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I. Abstract

Palintest released a new portable peracetic acid (PAA) monitoring device, Kemio, in summer of 2018. Enviro Tech Chemical Services, Inc. contacted Palintest and offered to perform a laboratory analysis and comparison to common test methods currently employed for the quantification of dilute PAA solutions. The Kemio proved to be accurate for quantification of the dilute PAA solutions (25-2000 mg/L) and is unaffected by the presence of hydrogen peroxide which is a common issues with current test methods. Additionally, Palintest's Kemio is less time consuming and more user friendly compared to conventional testing methods. After evaluation of various PAA products at various concentrations in 500 ppm CaCO3 AOAC synthetic hard water sources, Kemio is a useful method for analysis PAA products at use concentrations. Kemio demonstrates some technical and operational benefits compared to existing commonly used test methods.

II. Background

Peracetic acid is an organic peroxide that is primarily used as an antimicrobial intervention in food processing plants throughout the United States. While PAA has been used in the food industry for many years, it has become increasingly popular due to its efficacy, organic approval status, relatively short half-life, and safe disinfection byproducts. Most commercial PAA formulations are an equilibrium mixture of peracetic acid, hydrogen peroxide, and acetic acid (AA).

Currently, the most common test method for dilute PAA solutions is drop titration kits. The titration kits are iodometric titration. In this reaction, an oxidizer (such as PAA) oxidizes iodide to iodine, starch is used to indicate the presence of iodine, and then the iodine is titrated using sodium thiosulfate as a reducing agent to reduce the iodine back to iodide. This method has been adapted to small dropper-style titration kits that can be used in the field for dilute solutions of PAA. Currently there are two types of commercially available titration kits, uncatalyzed (4 reagent) and catalyzed (5 reagent). While both types kits are iodometric titrations, there are differences between the two different types of kits and the results can differ significantly. The uncatalyzed titration kits employ the use of three reagents and a single titrant which makes the uncatalyzed test kit more generalized and not as product specific. The iodometric test is a suitable test for many oxidizers and is not specific to PAA. Because of this, there is a problem: solutions of PAA also contain another oxidizer – hydrogen peroxide (HP). As it turns out though, HP reacts much slower with iodide than PAA. The uncatalyzed PAA titration kits make the assumption that HP reacts so much slower than PAA that the contribution to the test results can be ignored. With this assumption, the test result actually becomes a measurement of peracetic acid and some hydrogen peroxide. As a result, the uncatalyzed test kit typically reports higher PAA concentrations even though there is less PAA in a system due to the HP contributing to the results. This phenomenon is more extreme with PAA formulations that contain higher concentration of HP (≥10%) but is observed in varying degrees for all PAA products.

The catalyzed PAA titration kit employs a clever technique to "activate" the HP so it reacts with the iodine just as fast as the PAA. The test then measures the total amount of hydrogen peroxide and peracetic acid but correction factor (ppm per drop titrant) is adjusted based on the specific PAA product. The catalyzed PAA titration kits are product specific and should only be for specific PAA products that are listed on the instruction sheet. Catalyzed PAA test kits tend to be more consistent and report a more accurate PAA concentration since all the HP is taken into account and isn't contributing to the final results.

Palintest's Kemio is a novel testing unit that employs chronoamperometric technology which is specific for PAA regardless of the HP concentration. This means that Kemio is not product specific, eliminating potential errors from using the wrong titrant or ppm-per-drop correction factor. Because Kemio is electrochemical, it is unaffected by color, turbidity, and particulate or organic matter in the sample.

Kemio is much less cumbersome to use compared to conventional titration kits because it does not require the use of chemical reagents or counting and multiplying drops. The results are unbiased by operator technique or subjectivity, and log files make the results fully traceable. The Kemio can analyze PAA solutions ranging from 2-2000 ppm within 60 seconds without the need for dilution, making it suitable for almost every application of PAA.

III. Materials and Methods

A total of three different PAA products consisting of different PAA, HP, and acetic acid (AA) ratios were chosen for this validation study: Perasan A, BioSide HS 15%, and Perasan MP-2C (See Table 1).

Product	Lot #	% PAA	% HP	Avg. % AA
Perasan A	35-080218-1	5.75	26.68	6
BioSide HS 15%	33-080118-1	15.07	22.43	16
Perasan MP-2C	844-071818-1	22.58	4.98	45

Table 1 above lists the analysis results for PAA, HP, and the average AA in the three different PAA products used for this validation study.

Perasan A (lot# 35-080218-1)

Target PAA Conc. (ppm)	Water Volume (mL)	Dose (µL)
25	500	194
50	500	388
100	500	776
200	500	1552
500	250	1940
1000	250	3880
1500	200	4656
2000	200	6209

Table 2 above lists target PAA concentrations as well as the dose required for the Perasan A (35-080218-1).

BioSide HS 15% (lot# 33-080118-1)

Target PAA Conc. (ppm)	Water Volume (mL)	Dose (µL)
25	500	73
50	500	146
100	500	292
200	500	584
500	500	1462
1000	250	1462
1500	250	2193
2000	250	2923

Table 3 above lists target PAA concentrations as well as the dose required for the BioSide HS 15% (33-080118-1)

Perasan MP-2C (lot# 844-071818-1)

Target PAA Conc. (ppm)	Water Volume (mL)	Dose (µL)
25	1000	100
50	1000	200
100	1000	400
200	1000	800
500	1000	2000
1000	500	2000
1500	500	3000
2000	500	4000

Table 4 above lists target PAA concentrations as well as the dose required for the Perasan MP-2C (844-071818-1).

Test Method	Manufacturer	Item/Serial #
Uncatalyzed Test kit	AquaPhoenix	TK7500-Z
Catalyzed Test Kit	Masters Co.	D-10015-02
DPD-Meter[1]	Hach	DR-820
Kemio	Palintest	60305180009

Table 5 above lists the various test methods used to analyze the various PAA solutions as well as the manufacturer and model of the kits or units.

Samples analyzed via DPD were diluted to bring the concentration into the method's working range of 0.1-2.2 ppm.

Samples of 1000 ppm and above analyzed via drop count kits were diluted to preserve titrant and ensure sufficient quantity of acid, starch, and potassium iodide.

Theo. PAA Conc. (ppm)	Avg. PAA Conc. (ppm) (Perasan A)				n
	DPD Meter	Cata-lyzed Kit	Uncata-lyzed Kit	Kemio	
25	32.4	25.0	30.0	24.0	2
50	52.4	52.5	60.0	51.5	2
100	93.6	102.5	135.0	105.0	2
200	187.3	217.5	232.5	203.0	2
500	497.6	517.5	540.0	506.5	2
1000	952.3	1040.0	1170.0	1020.5	2
1500	1524.8	1455.0	1657.5	1510.0	2
2000	2075.8	2137.5	2257.5	2070.0*	2

*denotes that the sample was diluted 1:1 with deionized and the results multiplied by 2

Table 6 above compares the four different test methods for the quantification of various dilute PAA solutions from Perasan A.

Theo. PAA Conc. (ppm)	Avg. PAA Conc. (ppm) (BioSide HS 15%)				n
	DPD Meter	Cata-lyzed Kit	Uncata-lyzed Kit	Kemio	
25	26.2	22.8	37.5	25.5	2
50	51.9	49.0	72.5	50.5	2
100	100.0	96.3	120.0	102.0	2
200	208.7	180.5	225.0	206.5	2
500	465.5	479.5	532.5	489.5	2
1000	1150.3	1020.3	1065.0	1021.0	2
1500	1599.7	1484.0	1575.0	1515.5	2
2000	2054.4	2051.3	2115.0	2044*	2

*denotes that the sample was diluted 1:1 with

deionized and the results multiplied by 2

Table 7 above compares the four different test methods for the quantification of various dilute PAA solutions from BioSide HS 15%.

Theo. PAA Conc. (ppm)	Avg. PAA Conc. (ppm) (Perasan MP-2C)				
	DPD Meter	Catalyzed Kit	Uncatalyzed Kit	Kemio	n
25	32.6	30	30	28	2
50	49.8	50	65	51.5	2
100	108.1	105	112.5	104	2
200	228.4	195	202.5	198	2
500	502.9	500	525	509.5	2
1000	1177.0	1095	1027.5	1086.5	2
1500	1599.7	1495	1545	1515	2
2000	2081.2	1975	2052.5	1993	2

Table 8 above compares the four different test methods for the quantification of various dilute PAA solutions from Perasan MP-2C.

An additional analysis was performed to determine the impact that hydrogen peroxide alone has on the Kemio. Various HP solutions were generated using 50% hydrogen peroxide in deionized water. 50-mL of the various solutions were analyzed using the Kemio to determine if the HP is contributing to the PAA results which would lead to false high results.

Nominal HP Conc. (ppm)	Water Vol. (mL)	50% HP Dose (µL)	Kemio Results (ppm)
100	1000	170	<2
500	500	420	<2
1000	250	420	3.9
2000	150	500	5.7
3000	150	750	8.6

Table 9 above shows the impact of HP on the Kemio at various concentrations.

IV Conclusion

The goal of this study was to validate that the Kemio is a viable option for analyzing and quantifying dilute PAA solutions ranging from 25-2000 ppm in 500 ppm $CaCO_3$ AOAC synthetic hard water and compare the results to other common test methods currently employed. The other test methods were two different types of PAA drop titration kits (Catalyzed and Uncatalyzed), as well an electronic DPD meter. The two different types of test kits, catalyzed and uncatalyzed, showed noticeable different results which are explained by the differences in the test methods. As previously mentioned, the uncatalyzed test kit assumes the HP does not contribute to the final PAA results, but in formulations containing higher HP concentration (>10%, Perasan A and BioSide HS 15%), it is apparent that the uncatalyzed test kit produces higher PAA values compared to the catalyzed test kit that addresses the HP concentrations and subtracts it from the final results leading to a more accurate PAA result.

The results of this study suggest that the Kemio is an acceptable option for determining PAA concentrations between 25-2000 ppm accurately and precisely, plus it is relatively unaffected by the presence of 500 ppm $CaCO_3$ hardwater. The Kemio also demonstrated that it is unaffected by the HP present in PAA solutions leading to results that reflect the true PAA concentration. When comparing the results between the two different titration kits and the Kemio, the catalyzed test kit (Masters) results were more consistent with the Kemio than the results of the uncatalyzed test kit. This is most likely due to the breakthrough of the HP in uncatalyzed kit, leading to false-high reading of the PAA results. This phenomenon was more apparent with the Perasan A due to the HP concentration being significantly higher in the formulation. The results of the Perasan MP-2C were more consistent for all the test methods due to the formulation containing a much lower HP concentration.

Kemio's simplified digital technique combined with a direct on-screen concentration value makes this method particularly suitable for industrial applications. Kemio's methodology helps to remove operator and technique bias from results allowing consistency of analysis across staff and departments, while digital logging increases audit traceability.