

Validation of a Real-Time Peracetic Acid Vapor Sensor

December 5th, 2016

Joseph Donabed, B.S., Michael Harvey, B.S., Jon Howarth, Ph.D.
Enviro Tech Chemical Services, Inc.

Abstract

Currently ChemDAQ Inc. is the only company that has a commercially available real-time peracetic acid (PAA) vapor monitor. To date, there has been no publically available paper that validates the accuracy or precision of their sensor. In order to determine the accuracy and precision of the ChemDAQ PAA vapor sensor, Enviro Tech Chemical Services, Inc. developed a novel absorption column system that captures and solubilizes vapor phase PAA that is then able to be quantified. PAA vapor was generated from two distinctly different PAA formulations at various concentrations and the ChemDAQ PAA sensor measurements were compared to that of the absorption column design. The results of the study determined that regardless of the PAA formulation, the PAA vapor produced was virtually identical at equivalent solution concentrations. ChemDAQ's PAA vapor sensor proved to be a comparably accurate unit for measuring vapor phase PAA in real-time. The results from the PAA vapor sensor as well as the absorption column showed a strong linear correlation between PAA solution concentration and vapor production. ChemDAQ's PAA sensor correlated well with the results of the absorption column yielding a difference of $\leq 10.0\%$ between PAA solution concentrations of 25-100 ppm. There was no detectable interference from hydrogen peroxide or acetic acid. When the PAA solution concentration was increased to 250 ppm, there was a slight deviation (14.7% difference) between the absorption column method and the vapor sensor but this may be attributed to the PAA vapor phase concentration being near the upper end of the sensor's detection limit.

Background

Peracetic acid (PAA) 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. All PAA formulations are an equilibrium mixture of peracetic acid, hydrogen peroxide (HP), and acetic acid which produces a very pungent acetic acid (vinegar) odor that can make it very irritating to the eyes (lacrimation) and respiratory tract. PAA breaks down into naturally occurring compounds, hydrogen peroxide and acetic acid. The hydrogen

peroxide further breaks down to water while acetic acid will breakdown further to carbon dioxide (CO₂). Although PAA is relatively safe with respects to disinfection byproduct formation, care still needs to be taken when dealing with the concentrated product. When concentrated PAA comes into contact with skin, it can lead to temporary bleaching, burning sensation, redness, and itchiness. Prolong skin contact can lead to severe burns and even skin sloughing.

Acute exposure to concentrated PAA vapor in enclosed spaces can lead to watery eyes, runny nose, shortness of breath, and even burning of the trachea in severe cases. The Occupational Health and Safety Administration (OSHA) has established guidelines to limit the amount of

exposure of hazardous chemicals and pollutants to employees during any given work day. While OSHA and the CDC/NIOSH do not currently have a final exposure limit for peracetic acid, the ACGIH does have recommendations. This recommendation was disclosed with their 2015 publication which set a STEL (Short Term Exposure Limit) of 0.4 ppm (IFV) with an A4 notation stating: NOT CLASSIFIABLE AS A HUMAN CARCINOGEN. Typically, employees are exposed to PAA vapor produced from diluted PAA solutions (<1000 mg/L) unless they are dealing with spills of the concentrated solution. At lower solution concentrations, the vapor phase production is relatively limited and usually does not cause ill effects unless an individual exhibits hypersensitivity to PAA.

ChemDAQ Inc. (Pittsburgh, PA), has the only commercially available real-time PAA vapor sensor technology. That PAA vapor sensor technology has been incorporated in both the ChemDAQ Steri-Trac® and SafeCide™ units. To date, there has been no publically available paper that validates the accuracy or precision of the ChemDAQ PAA vapor sensor technology. The purpose of this study is to determine the accuracy of ChemDAQ's PAA vapor sensor with respects to quantification of PAA vapor concentrations using two markedly dissimilar PAA formulations.

In order to determine if ChemDAQ's PAA vapor sensor is monitoring vapor-phase PAA accurately, another test method was developed by Enviro Tech Chemical Services, Inc. to use as a comparison. An absorption column system was developed by Enviro Tech that allows produced PAA vapor to be contained and then solubilized in water. The water containing the dissolved PAA vapor would then be analyzed in order to determine the amount of PAA vapor that was

produced given the known volume of air that was sparged into a PAA solution and passed through the absorption column.

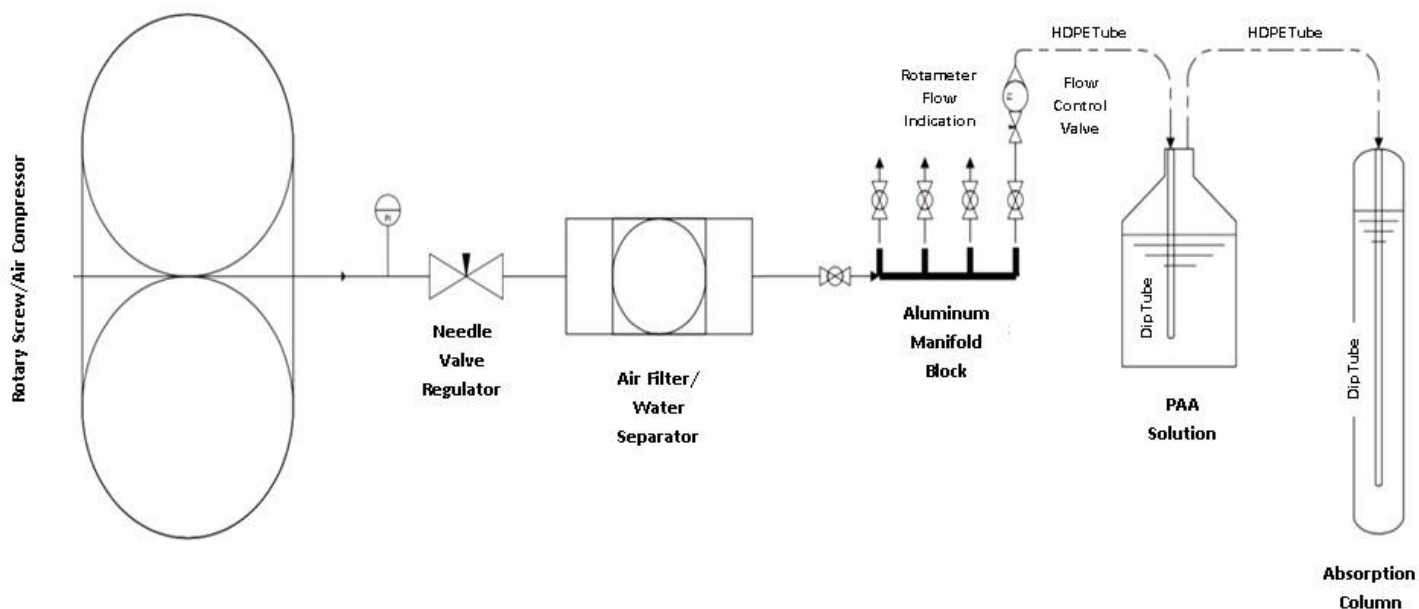
The ChemDAQ device provides a numerical measurement of the PAA vapor phase concentration in ppm employing electrochemical (amperometric) principles. The vapor phase PAA is electrochemically reduced at an electrode. The magnitude of the reduction current that is measured is directly proportional to the amount of PAA that is present in the vapor.

Materials and Methods

Absorption Column Experimental Design

A Cole-Parmer 0.1-1 LPM acrylic air flowmeter (Item # EW-32460-42) was connected to a rotary screw air compressor. A standard air filter was placed in-line to reduce moisture prior to passing through the flowmeter. Two holes were drilled in a number 5 black rubber stopper and using two Falcon® serological 1 in 1/100 mL pipette, the rubber stopper was fitted with an inlet and outlet. Then, ¼ inch HDPE tubing was connected from the flowmeter to the inlet pipette. The outlet pipette was fitted with ¼ inch HDPE tubing approximately 45 inches in length. The modified stopper was fitted into a 1000 mL round flask (24/40). Next, a CPVC pipe (2 x 36 inches) was capped at one end and filled with approximately 1600 mL of reverse osmosis water which would serve as an absorption column (See [Figure 1](#)). The column water was tested prior to the start of each study to verify it was oxidant free. Two different Enviro Tech peracetic acid products

Figure 1 is a schematic of the absorption column experimental design.



were chosen for this study, BioSide HS 15% and Perasan MP-2C.

Table 1 lists the percentages of the peracetic acid, hydrogen peroxide, and acetic acid in the BioSide HS 15% and Perasan MP-2C

Product	% PAA	% H ₂ O ₂	% Acetic Acid
BioSide HS 15%	15.2	22.0	16.0
Perasan MP-2C	22.0	5.0	45.0

Using the BioSide HS 15% and the Perasan MP-2C, four nominal PAA solutions were made, 25, 50, 100, and 250 ppm. Approximately 500 mL of each PAA solution was transferred to the 1000 mL round flask. The stopper was fitted on the flask with the sparge tube being submerged approximately 1 cm into the PAA solution. The air flowmeter was turned on and set at 1 LPM. The system was purged for 10 minutes to equilibrate the PAA vapor production. After the system was purged, the HDPE tube was submerged to the bottom of the 36 in. absorption column and a

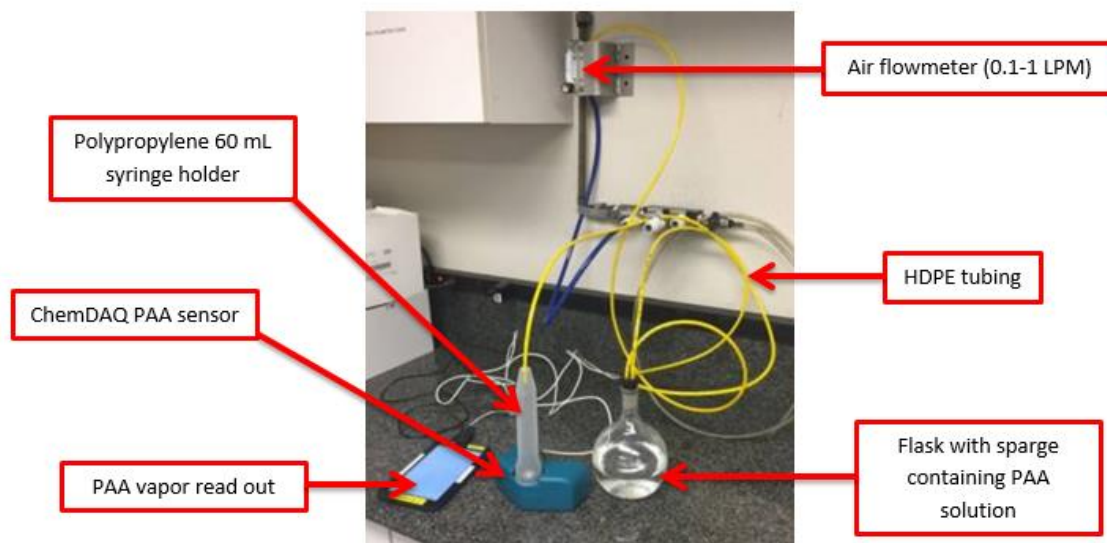
timer was started. Aliquots were taken at various time intervals and analyzed for PAA using the Modified Palin DPD methodology (Enviro Tech US Patent 7,651,860 B2). The concentration of PAA was quantified in the absorption column over a period of time. The data obtained from the analysis of PAA in the absorption column was then used to determine to vapor phase concentration based on the 1 LPM air flow.

ChemDAQ's PAA Vapor Sensor Experimental Design

The same experimental setup was used to test the PAA vapor sensor unit but instead of the absorption column, the PAA vapor that was produced was directed to the PAA vapor sensor using a polypropylene 60 mL syringe holder (See Figure 2). The sensor was connected to a Winbook model TW700, running Windows 8.1. The output from the sensors is a proprietary 485 signal. The sensor was connected to the tablet via a 485/USB converter. The PAA air sensor was covered for approximately 120 seconds until the

concentration reading stabilized. The data was collected using ChemDAQ's data log software and results were manually recorded.

Figure 2 shows the experimental design for the ChemDAQ PAA vapor sensor unit.



the entire amount of PAA vapor produced was solubilized in the absorption column, the mass of PAA produced in the vapor could be back calculated using the concentration of PAA (mg/L) in the absorption column. Since multiple concentration readings were taken over 60-180

Once the data collection was completed for the absorption column, the PAA vapor was then directed to the ChemDAQ PAA sensor unit and the results obtained were compared to that obtained from the absorption column.

Results and Discussion

It was initially hypothesized that the PAA vapor production would be different between the two PAA formulations at the same concentration potentially due to the differences in partial pressures, but the PAA vapor generation between the two different formulations were virtually identical. Therefore, the results obtained from the absorption column and the ChemDAQ PAA vapor sensor for the two different PAA products at the same nominal concentrations were averaged and plotted.

The PAA solution concentration was analyzed using the Palin Modified DPD Methodology. Assuming that

minute time interval and the air flow was set at 1 LPM, the accumulation of PAA mass over time from the vapor phase could be determined. A graph was generated by plotting the mass of PAA (mg) produced in the in the vapor over time which showed strong linearity at all concentrations tested. A trendline was fitted to the points on the graph and a standard $y = mx + b$ equation was generated. The slope of the line would be the average mass of PAA produced (mg) in the vapor phase and the ppm of PAA vapor was determined using the following equation:

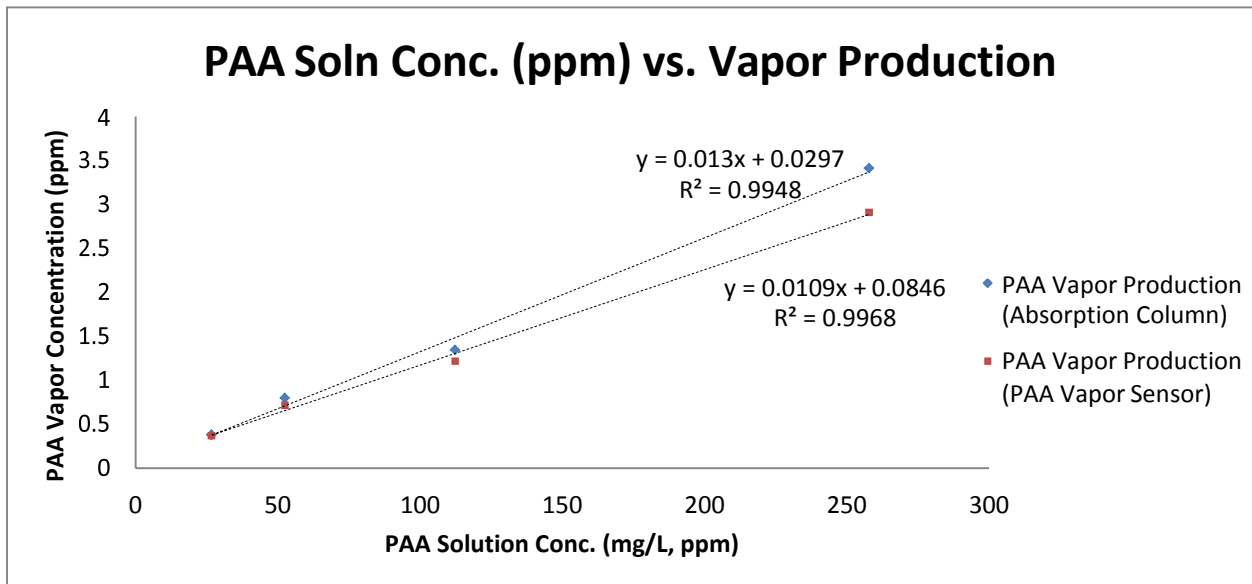
Equation 1 shows the calculation for ppm PAA vapor.

$$ppm \text{ PAA Vapor} = \frac{(\text{slope} \times 1000) \times 24.45}{mw \text{ PAA}}$$

Table 2 compares the vapor concentration readings from the absorption column and ChemDAQ PAA vapor sensor.

PAA Solution Conc.	Absorption Column Conc. (ppm)	ChemDAQ Vapor Conc. (ppm)	% Difference Between Absorption Column and Sensor
26.75	0.38	0.37	+2.6
52.43	0.80	0.72	+10.0
112.35	1.35	1.22	+9.6
257.91	3.41	2.91	+14.7

Figure 3 compares the PAA vapor production from two distinctly different PAA formulations using the absorption column design and the ChemDAQ PAA vapor sensor.



The absorption column showed excellent linearity over the 25-250 ppm PAA range yielding a correlation coefficient (R^2) of 0.9948. The linearity of the absorption column results demonstrates that the PAA vapor produced was completely solubilized in the absorption column as well as showing that regardless of the PAA formulation, the vapor production is virtually identical. An absorption column length of 36 inches was arbitrarily chosen but, based on the results of this study and the solubility of PAA, a shorter absorption column may achieve the same results.

The results of ChemDAQ's PAA vapor sensor also showed excellent linearity over the 25-250 ppm PAA range yielding a correlation coefficient (R^2) of 0.9968. The results from the ChemDAQ PAA vapor sensor correlated well with the absorption column yielding a difference of $\leq 10.0\%$ between nominal PAA solution concentrations of 25-100 ppm from two different PAA formulations. When the PAA solution concentration was increased to a nominal 250 ppm, the PAA vapor concentration was 2.91 ppm in the absorption column and 3.41 ppm PAA using the ChemDAQ PAA vapor sensor. This equates to a 14.7% difference between the two

different methods. The ChemDAQ PAA vapor sensor has a published detection range of 0-3 ppm PAA therefore, the deviation between the two methods at the higher PAA solution concentration may be attributed to being at the upper end of the detection limit for the ChemDAQ PAA vapor sensor.

Conclusion

The novel absorption column design proved to be a simple and accurate method for quantifying PAA vapor. Two vastly different PAA formulations were tested in this study which yielded very similar results which suggests that while PAA is always in equilibrium with acetic acid and hydrogen peroxide, PAA vapor detection is not influenced by the presence of the other two molecules or apparent vapor pressure differentials. The absorption column also verified that there is a strong linear correlation between PAA solution concentration and vapor production when subjected to substantially identical experimental conditions.

ChemDAQ's PAA vapor sensor proved to be a comparably accurate unit for measuring vapor phase PAA in real-time. The results from the PAA vapor sensor showed a strong linear correlation between PAA solution concentration and vapor production. ChemDAQ's PAA sensor correlated well with the results of the absorption column yielding a percent difference of $\leq 10.0\%$ between PAA solution concentrations of 25-100 ppm. When the solution concentration of PAA was increased to 250 ppm, there was a slight deviation (14.7% difference) between the absorption column method and the vapor sensor but this may be attributed to the PAA vapor phase concentration being right at the upper end of the sensor's detection limit.

One of the most significant findings of this study was that the ChemDAQ PAA sensor was selective

for PAA only and proved to be unaffected by hydrogen peroxide and acetic acid. The PAA sensor is equipped with a chemical filter that selectively removed vapor phase hydrogen peroxide ensuring that the results are representative for PAA only.

The results of this study suggest that the ChemDAQ unit accurately measured vapor phase PAA up to 3 ppm in real-time and appears to be unaffected by both hydrogen peroxide and acetic acid vapor.

It is important to note that the results obtained in this study are based on laboratory experimental conditions. In actual use applications, there are a variety of variables that play a factor in PAA vapor evolution and detection. Common variables are atmospheric temperature and pressure, PAA solution temperature, volume of PAA solution, degree of agitation, ventilation, room size, and distance from PAA solution.