MEASUREMENT OF VIGOROX® WWT II PERACETIC ACID IN WASTEWATER

VigorOx® WWT II Wastewater Disinfection Technology

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Accurate measurement of peracetic acid (PAA) in wastewater is critical for the proper dosing of PAA to meet target microbial reduction targets and to ascertain the concentration of PAA in the plant effluent to meet local regulatory water quality standards. This edition of Wastewater Disinfection Forum discusses the current state of the art in the measurement of PAA in municipal wastewater.

I. QUANTITATIVE CHEMICAL ASSAY OF PERACETIC ANALYSIS

Quantitative analysis of peracetic acid (PAA) in wastewater is performed using the "DPD" method, which is analogous to the US EPA Method 330.5[1] for the determination of chlorine concentration. In this method, the sample containing PAA is treated with an excess of potassium iodide (KI). The peracetic acid oxidizes the iodide to iodine. The iodine subsequently oxidizes the DPD (N,N-diethyl-p-phenylelnediamine) to a pink colored species. The pink color will be in direct proportion to the amount of peracetic acid in the sample and can be quantified via comparison to a color chart or measured via photometer.

DPD kits and photometers are commercially available. Evonik recommends the CHEMetrics I-2020 Single Analyte Meter (SAM). The SAM photometer comes pre-calibrated by the manufacturer to correlate for their "activator solution". If a different photometer is utilized, then the following equation to correlate color absorbance (abs) to PAA concentration (ppm) is used:[2]

$$ppm = 0.92\,(abs^2) + 4.84\,(abs) - 0.01$$

II. INTERFERENCES

Peracetic acid solution is an equilibrium mixture of peracid acid, hydrogen peroxide and acetic acid. Hydrogen peroxide will not interfere with the DPD test method if the peroxide is in the same general concentration range as the peracetic acid. For VIGOROX® WWT II, the hydrogen peroxide and peracetic acid will be in the same general concentration range. Various oxidants, such as halogens, ferric ions and cupric ions can induce interference with the method, producing high test results. As a result, these interferences will bias against a PAA residual exceeding the site permitted value.

Incorporation of a "blank" measurement will help to eliminate the impact of interference from wastewater constituents. The blank measurement consists of running a DPD test on a sample of the wastewater without the PAA being added. Any subsequent absorbance measurement from the blank sample can then be subtracted out of the PAA test sample, proving a more accurate quantification of PAA in the wastewater.

III. ACCURACY OF THE DPD METHOD

The I-2020 SAM system is listed as accurate to ± 20% at the low end of the detection range and ± 30% at the detection limit[2]. At the behest of Evonik, Hydroqual HDR performed an investigation into the accuracy of the SAM unit[3]. A series of PAA solutions were prepared with pre-determined PAA concentrations from 0.1 to 4 ppm. A SAM analyzer was used by three technicians to measure the PAA concentrations of these PAA solutions. Each solution was subjected to ten replicate measurements by each technician. The measurements were grouped per expected PAA concentrations, and the standard deviation of all measurements per PAA concentration was analyzed against the mean measured PAA concentration. The maximum uncertainty in the SAM measurement was then determined by the boundary of the confidence interval as set by the standard deviations of the measurements. A regression analysis was conducted to correlate the SAM measurement uncertainty as a function of mean PAA concentration. This correlation is expressed as:

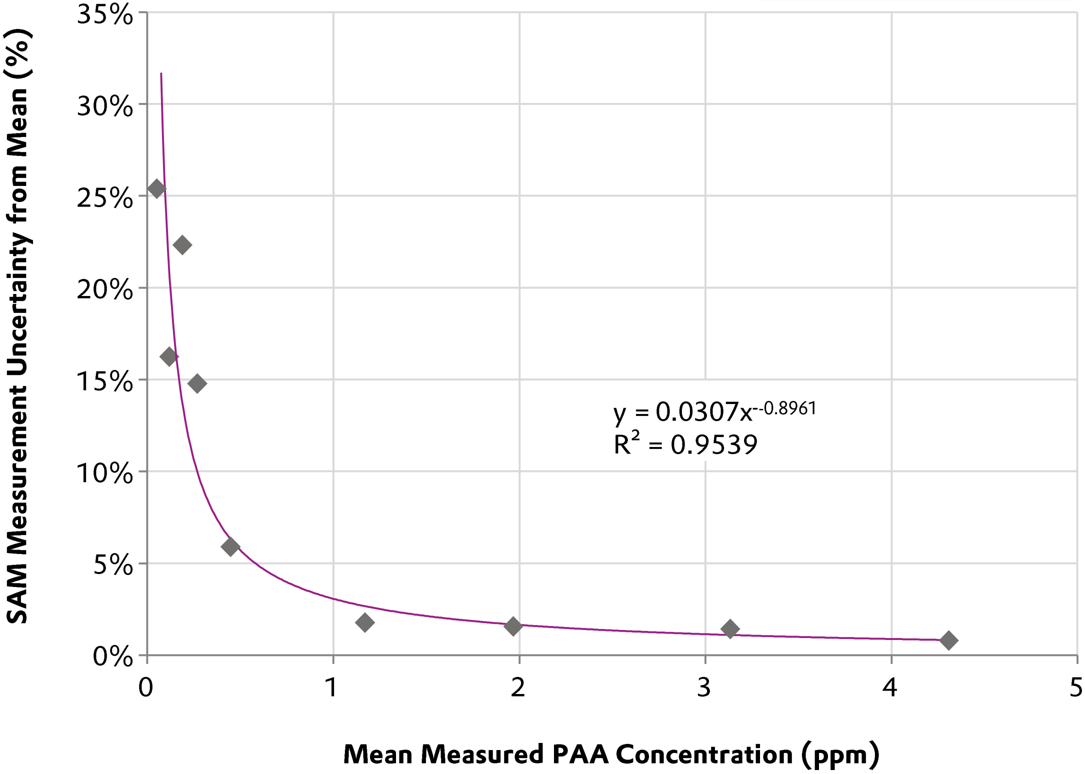
$$SAM\ measurement\ uncertainty = 0.0307\ * PAA\ concentration\ (ppm)^{-088961}$$

and displayed in Figure 1. In general, the SAM unit is accurate to:

Figure 1

SAM Measurement Uncertainty as a Function of Measured PAA Concentration

± 3% at 1.0 ppm PAA
± 6% at 0.50 ppm PAA
± 15% at 0.25 ppm PAA



IV. ON-LINE, REAL TIME PAA MEASUREMENT

On-line, real time, continuous measurement of peracetic acid is achievable by commercially available in situ probes. The ProMinent DulcoTest® CTE peracetic acid probe is a membrane-capped, amperometric, twoelectrode censor for continuous measurement of PAA in wastewater. The probe is calibrated using the CHEMetrics I-2020 Single Analyte Meter (SAM) to provide the reference PAA concentration. Calibration is done on a scheduled, periodic basis, typically once every week or two. Additional calibration is performed if the measured PAA concentration by the probe is ± 20% different than the concentration as determined by the SAM unit.

As with the SAM unit, HydroQual HDR performed a study[2] investigating the accuracy of the PAA probe under real wastewater conditions. Two PAA probes were investigated and the probes demonstrated general agreement with their corresponding SAM measurements, as seen in Figure 2. The overall uncertainty associated with the PAA probe measurement is shown in Figure 3.
In general, the amperometric PAA probe is accurate to:

Figure 2

Probe Reading Versus SAM Reading

± 3% at 1 ppm PAA
± 8% at 0.5 ppm PAA
± 15% at 0.25 ppm PAA

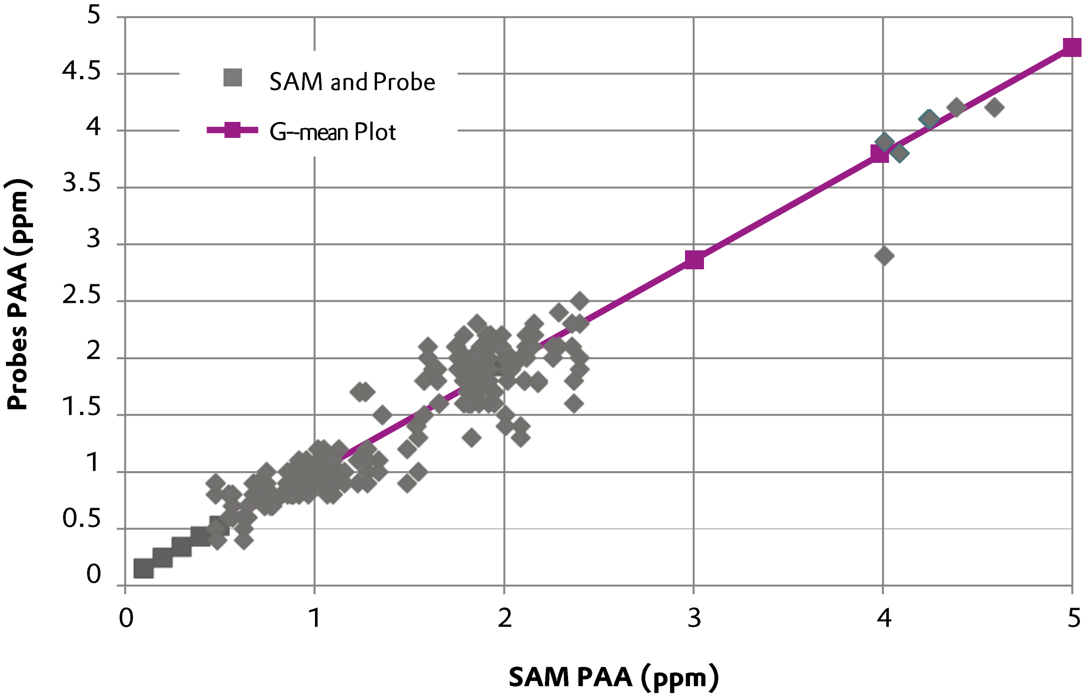
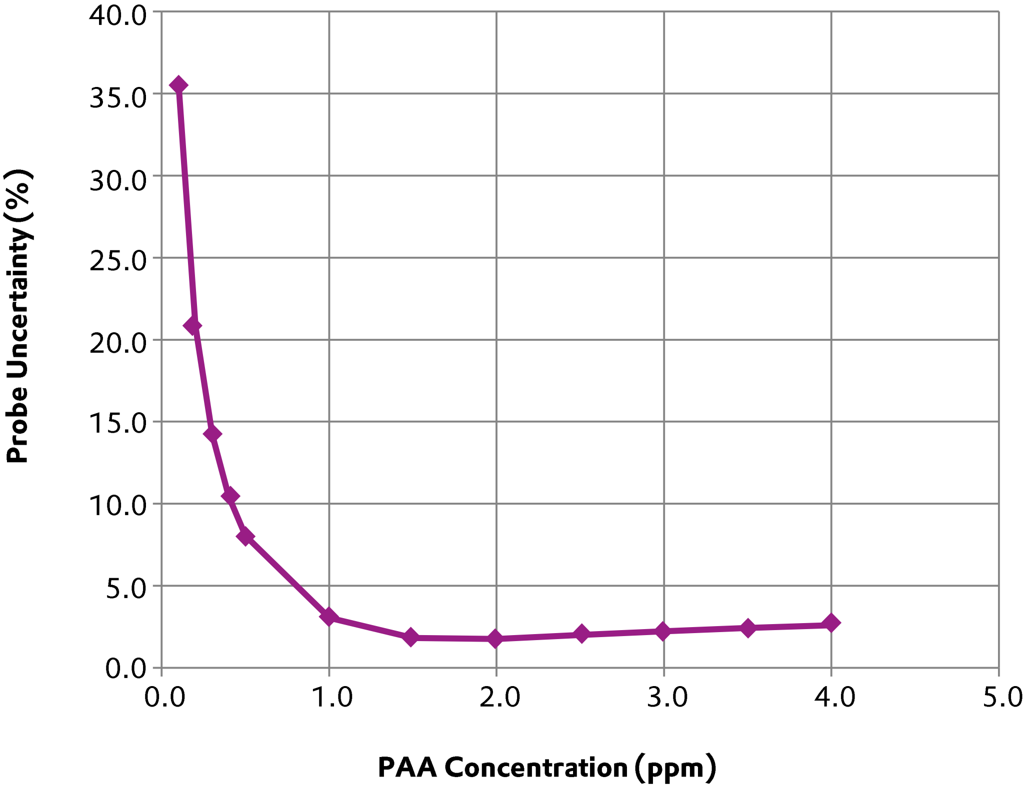


Figure 3

Amperometric Probe Uncertainty as a Function of PAA Concentration



METHODS

(1) “Methods for Chemical Analysis for Water and Wastes.” US EPA (1983).

(2) CHEMetrics. Peracetic Vacu-Vials® Kit test method. www.chemetrics.com.

(3) Validation of PeroxyChem In-Line Peracetic Acid Monitoring Probe. Internal report generated by HydroQual HDR (2014).

PeroxyChem LLC
2005 Market Street,
Suite 3200,
Philadelphia, PA 19103
United States

+1 267 422 2400
www.active-oxygens.com