

Validation of a Method to Determine Peroxyacetic Acid (PAA) and Hydrogen Peroxide (PERASAN[®], EPA #63838-2) at Levels Used in the Treatment of Wastewater

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 7 JANUARY, 2004

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I. Introduction

A number of companies supply reagent test kits for the determination of peroxyacetic acid and hydrogen peroxide in water. Some are based on test strips consisting of a pad impregnated with an indicator reagent that changes color in response to the concentration of the analyte¹. The user dips the test strip in the water for a few seconds and compares the color response to a comparator chart. Although test strips are convenient to use, they are insufficiently accurate for reliable measurements. Another test kit is based on the ceric IV sulfate – sodium thiosulfate reaction that employs a ferroin indicator². This technique can only be used when the concentration of the peroxyacetic acid is greater than 30 ppm and hydrogen peroxide is greater than 100 ppm. A commercially available test kit based on DDPD (methyl-substituted N,N-diethyl-p-phenylenediamine) boasts a much lower detection limit of 0.5 ppm peroxyacetic acid³. In this method the analyst treats the sample with an excess of potassium iodide. A one minute reaction time permits the peroxyacetic acid to oxidize the iodide to iodine. The sample is then introduced to methyl-substituted N,N-diethyl-p-phenylenediamine indicator, which forms a purple coloration in direct proportion to the peroxyacetic acid concentration. Color comparator tubes or a pre- calibrated spectrophotometer set to 565 nm are used quantitate the amount present. Enviro Tech Chemical Services has used this technique many times and found it to possess a number of limitations. For example, although it provides reliable and reproducible results in de-ionized water, the opposite is true in natural waters, even clean drinking water. The reasons for this unpredictability are uncertain. Several scientific papers have been published^{4,5} which document other analytical techniques for determining

hydrogen peroxide and peroxyacetic acid but these are not commercially available and employ exotic reagents and expensive instrumentation.

Peroxyacetic acid-hydrogen peroxide equilibrium products are currently under consideration in the USA as chlorine alternatives in wastewater disinfection. In order for these products to be permitted in these applications, the results of aquatic toxicology tests, efficacy tests and field trial results must be presented to government regulatory agencies. Without a simple, accurate, reliable and readily available test procedure for peroxyacetic acid and hydrogen peroxide, the results of such test are meaningless. This report describes the development of a procedure that meets such criteria.

The present analytical technique is based on the US EPA-accepted DPD (N,N-diethyl-p- phenylenediamine) colorimetric method for measuring total chlorine in drinking water and wastewater. It relies on the ability of peroxyacetic acid (PAA) to behave like chlorine in that it rapidly and quantitatively oxidizes iodide ion (I⁻) into iodine (I₂) that reacts with a color indicator (DPD), which turns the solution a shade of pink, the intensity of which is proportional to the concentration of the PAA. A colorimeter is used that is programmed to measure the intensity (absorbance) of the pink coloration and display the result in terms of ppm as Cl₂. A simple calculation converts this number into the ppm as PAA, based on the weight ratio of PAA to Cl₂ (76/71).

Hydrogen peroxide does not interfere with the measurement for PAA provided, the analysis is completed within 30 seconds of introducing the DPD reagent. In order for the hydrogen

peroxide to be measured, it must be activated by addition of a catalyst and then given time to react with the I⁻ ion to liberate I₂. Upon addition of the DPD indicator, the intensity of the pink coloration measured by the colorimeter is now the sum of the PAA and hydrogen peroxide concentrations expressed as ppm Cl₂. After subtracting the contribution due to PAA, a simple calculation is then used to convert this number into ppm as H₂O₂, and is based on the weight ratio of H₂O₂ to Cl₂ (34/71).

II. Method Development and Evaluation

II.i.EXPERIMENTAL

The standard 0.1N ceric IV sulfate – 0.1N sodium thiosulfate/iodometric analytical technique was used to determined that a freshly prepared batch of Perasan contained 15.55% peroxyacetic acid, and 22.3% hydrogen peroxide. This was used to prepare a stock solution containing 100 ppm PAA and 143.4 ppm H₂O₂ by weighing 0.323g into a 500 ml volumetric flask and making up to volume with deionized water. The freshly prepared solution was used to dose a moderately hard EPA reconstituted water (see reference 8 for details) possessing the water quality parameters listed in Table I.

The first solution prepared was dosed to contain a nominal concentration of 2.0 ppm PAA and 2.87 ppm H₂O₂. This was immediately analyzed for PAA and H₂O₂ using the DPD methods listed in the Appendix. A total of 5 replicates were made. Thereafter, further dilutions were prepared and the process was repeated for each dilution. Table II reports the number of dilutions that were made, along with their nominal concentrations of PAA and H₂O₂.

TABLE I

| | pH | Conductivity μS/cm ⁻¹ | Total alkalinity/ ppm as CaCO ₃ | Total hardness/ ppm as CaCO ₃ |
|---------------------------|-----|-------------------------------------|---|---|
| Moderately hard EPA water | 7.3 | 341 | 60 | 74 |

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TABLE II

| Dilution in Moderately Hard EPA water | Nominal dose of PAA /ppm | Nominal Dose of H ₂ O ₂ /ppm |
|---------------------------------------|--------------------------|--|
| 1 | 2.00 | 2.87 |
| 2 | 1.00 | 1.43 |
| 3 | 0.5 | 0.72 |
| 4 | 0.25 | 0.36 |
| 5 | 0.1 | 0.14 |
| 6 | 0.05 | 0.07 |

The data was entered into a Microsoft Excel Spreadsheet for statistical analysis.

II.ii. STATISTICAL ANALYSIS

Table III records the mean concentration of PAA, residual standard deviation, and % recovery for the diluted solutions prepared in EPA reconstituted water.

TABLE III

| Nominal Concentration / ppm PAA | Mean Recovered Concentration / ppm PAA | Relative Standard Deviation | % Recovery |
|---------------------------------|--|-----------------------------|------------|
| 2.00 | 1.988 | 0.027749 | 99.4 |
| 1.00 | 1.006 | 0.015166 | 100.6 |
| 0.50 | 0.516 | 0.018166 | 103.2 |
| 0.25 | 0.246 | 0.008944 | 98.4 |
| 0.1 | 0.095 | 0.009815 | 95.0 |
| 0.05 | 0.051 | 0.015945 | 102.0 |

Regression analysis software was used to calculate a correlation coefficient (R²) of 0.9995, and the following mathematical relationship:

$$\text{Measured ppm of PAA (Y)} = 0.9954 \times \text{Nominal ppm PAA (X)} + 0.0034$$

Figure 1 depicts this information graphically. The line through the data point represents the above equation, and is the best fit to the data calculated using the linear-least squares method.

Table IV records the mean concentration of H₂O₂, residual standard deviation, and % recovery for the diluted solutions prepared in EPA reconstituted water.

TABLE IV

| Nominal Concentration / ppm H ₂ O ₂ | Mean Recovered* Concentration / ppm | Relative Standard Deviation | % Recovery |
|---|-------------------------------------|-----------------------------|------------|
| 2.87 | 2.59 | 0.021008 | 89.0 |
| 1.43 | 1.36 | 0.066156 | 98.6 |
| 0.72 | 0.65 | 0.014832 | 90.0 |
| 0.36 | 0.36 | 0.021008 | 99.4 |
| 0.14 | 0.17 | 0.01034 | 120.7 |
| 0.07 | 0.11 | 0.013038 | 185.7 |

*Recoveries rounded to two significant figures.

Regression analysis software was used to calculate a correlation coefficient (R²) of 0.9968 and the following mathematical relationship:

$$\text{measured ppm of H}_2\text{O}_2 \text{ (Y)} = 0.912 \times \text{nominal ppm H}_2\text{O}_2 \text{ (X)} + 0.015$$

Figure 2 depicts this information graphically. The line through the data point represents the above equation, and is the best fit to the data calculated using the linear-least squares method.

III. Results and Discussion

Regression analysis of the data indicates that the DPD total chlorine method is extremely satisfactory for selective and accurate analysis of peroxyacetic acid. Over the concentration range 0.05 – 2.00 ppm, analytical recoveries were close to quantitative in all cases.

Colorimeters programmed to respond to the presence of chlorine are suitable for the determination of PAA, and are available from a variety of manufacturers, making this method very amenable for common use. Due to the molecular weight difference between Cl_2 and PAA (71 and 76, respectively), the result that is displayed is simply multiplied by 1.07 (76/71) to convert ppm Cl_2 into the equivalent result for PAA.

A correlation coefficient of 0.9995 indicated that there was no interference from hydrogen peroxide also present in solution. This is attributed to the fact that the analysis takes place rapidly in the colorimeter within 30 seconds of contact with the DPD/KI indicator.

Hydrogen peroxide, on the other hand, only responds in the presence of a molybdate catalyst and following a 6 minute reaction time.

The DPD/KI colorimetric method for analysis using the total chlorine technique described herein is reported^{6,7} to have a standard deviation of 0.012 ppm as Cl_2 , equivalent to 0.0128 ppm as PAA. By definition in standard methods⁷, the minimum detection limit is established at three times the standard deviation. However, in order to build as much safety margin into the method to account for its use under non-ideal conditions and in a variety of water matrices, it is recommended that the minimum detection limit (MDL) of PAA using this method be set to 0.04 ppm.

Regression analysis of the data indicates that the DPD total chlorine method is not quite as accurate and selective for the determination of hydrogen peroxide as it is for peroxyacetic

acid. Nevertheless, over the concentration range 0–2.97 ppm, analytical recoveries were satisfactory at all but the lowest concentration employed. A correlation coefficient of 0.9968 indicates the suitability of the technique for accurate and reliable analysis.

Colorimeters programmed to respond to the presence of chlorine are suitable for the determination of H_2O_2 , and are available from a variety of manufacturers, making this method very amenable for common use. Due to the molecular weight difference between Cl_2 and H_2O_2 (71 and 34, respectively), the result that is displayed is simply multiplied by 0.478 (34/71) to convert the ppm Cl_2 into the equivalent result for H_2O_2 , *after* subtracting the PAA contribution to the response.

The DPD/KI colorimetric method for analysis using the total chlorine technique described herein is reported^{6,7} to have a standard deviation of 0.012 ppm as Cl_2 , equivalent to 0.005 ppm as H_2O_2 . By definition in standard methods⁷, the minimum detection limit is established at three times the standard deviation. However, in order to build as much safety margin into the method to account for its use under non-ideal conditions and in a variety of water matrices, it is recommended that the minimum detection limit (MDL) of H_2O_2 using this method be set to 0.02 ppm.

IV. Main Findings

- Using the DPD total chlorine method permits quantitative recovery of PAA, and regression analysis of the data reveals a correlation coefficient of 0.9995.
- In combination with a Hach Model 46700-00 pocket colorimeter, the DPD total chlorine method permits PAA to be measured with a minimum detection level (MDL) of 0.04 ppm under end-user, practical or laboratory conditions.
- Hydrogen peroxide does not interfere with the analysis of PAA.
- Using the DPD total chlorine method with a molybdate catalyst permits excellent recovery of H₂O₂, and regression analysis of the data reveals a correlation coefficient of 0.9968.
- In combination with a Hach Model 46700-00 pocket colorimeter, the DPD total chlorine method + molybdate catalyst permits H₂O₂ to be measured with a minimum detection limit (MDL) of 0.02 ppm under end-user, practical or laboratory conditions.
- The US EPA-accepted DPD (N,N-diethyl-*p*-phenylenediamine) colorimetric method for measuring total chlorine in drinking water and wastewater has previously been validated and accepted by the EPA. This sub-method of the DPD indicator procedure can now be validated for the determination of peroxyacetic acid (0-2 ppm) and hydrogen peroxide (0-2.87 ppm).

V. References

- ⁽¹⁾ Peroxide Test Strips. Precision Laboratories, West Chester, OH 45071
- ⁽²⁾ Peracetic Acid Test Kit. Code 7191-01. LaMotte Co. Chesterton, MD 21620
- ⁽³⁾ Peracetic Acid Single Analyte Meter. CHEMetrics Inc., Calverton, VA 20138
- ⁽⁴⁾ *Disinfection of Wastewater by Hydrogen Peroxide or Peracetic Acid: Development of Procedures for Measurement of Residual Disinfectant and Application to a Physicochemically Treated Municipal Effluent.* M. Wagner, D. Brumelis, R. Gehr. Water Environment Research **74**(1) p.33 (2002)
- ⁽⁵⁾ *Electroanalysis of Peracetic Acid in the Presence of a Large Excess of Hydrogen Peroxide.* Awad, M. I.; Harnood, C.; Tokuda, K.; Ohsaka, T. Analytical Letters **34** (7) p.1215-1221 (2001)
- ⁽⁶⁾ Water Analysis Handbook. 2nd Edition. Hach Company. Loveland, Co 80539
- ⁽⁷⁾ Standard Methods for the Examination of Water and Wastewater. 20th Edition. Part 4 p.63. APHA, AWWA, WEF (1998)
- ⁽⁸⁾ *Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms: EPA/600/4-91/002, 3rd Edition.*

Appendix A Figures 1 and 2

FIGURE 1: NOMINAL VS. MEASURED PAA CONCENTRATION

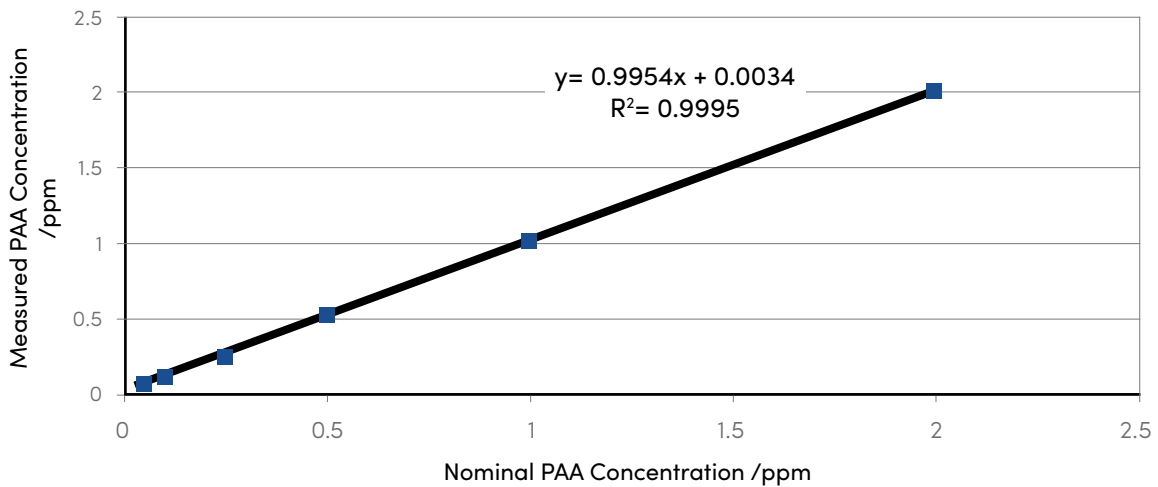
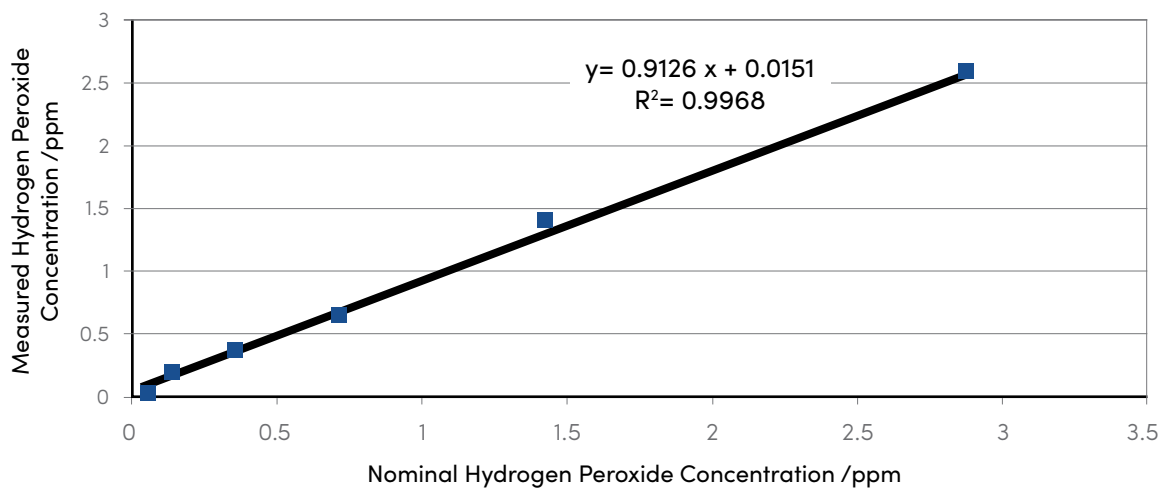


FIGURE 2: NOMINAL VS. MEASURED HYDROGEN PEROXIDE CONCENTRATION



Appendix B:

DETERMINATION OF PERACETIC ACID (PAA) AND HYDROGEN PEROXIDE (H₂O₂) IN WATER

EQUIPMENT AND REAGENTS

Chlorine – Pocket Colorimeter. Hach Model 46700-00
DPD TOTAL Chlorine Reagent Powder Pillows for 10 ml sample size. Hach Product number 21056-69. **Important note:** Do **NOT** use DPD FREE Chlorine Reagent Powder Pillows.

- Hydrogen Peroxide Activator 1 (15% KI solution)
- Hydrogen Peroxide Activator 2 (5% ammonium molybdate solution)

PROCEDURE FOR PAA

Before testing, make sure the instrument is in the low (LO) range mode by checking that the display reads to hundredths (0.00)

Note: the sample must be analyzed immediately, as it cannot be preserved for subsequent analysis.

- (1) Fill both 10 ml sample cells with the water sample. Designate one of these to be the blank and one to be the prepared sample.
- (2) Add the contents of one DPD TOTAL Chlorine powder pillow to the prepared sample cell.
- (3) Cap the prepared sample cell and shake gently to mix the DPD powder. A pink color will develop indicating the presence of PAA.
- (4) Within 30 seconds of adding the DPD powder to the prepared sample cell, cap the blank cell and place it in the cell holder with the diamond mark facing you. Cover the cell compartment with the instrument cap to shield from stray light interferences and then press ZERO.
- (5) The instrument will turn on and the display will show --- then 0.00. Remove the blank cell and replace it with the prepared sample cell. Align the cell and cover the cell compartment and then press READ.
- (6) The instrument display will show --- followed by the results in ppm total chlorine. This is the ppm total Cl₂ PAA value

CALCULATION

$$\text{ppm PAA} = 1.07 \times \text{ppm total Cl}_2 \text{ PAA}$$

PROCEDURE FOR HYDROGEN PEROXIDE

Before testing, make sure the instrument is in the low (LO) range mode by checking that the display reads to hundredths (0.00)

Note: the sample must be analyzed immediately, it cannot be preserved for subsequent analysis.

- (1) Fill both 10 ml sample cells with the water sample. Designate one of these to be the blank and one to be the prepared sample.
- (2) Add 3 drops of Hydrogen Peroxide Activator 1 and 3 drops of Hydrogen Peroxide Activator 2 to the prepared sample cell.
- (3) Swirl the prepared sample cell to mix and let react for 6 minutes.
- (4) Then, add the contents of one DPD TOTAL Chlorine powder pillow.
- (5) Cap the prepared sample cell and shake gently to mix the DPD powder. A pink color will develop.
- (6) Within 30 seconds of adding the DPD powder to the prepared sample cell, cap the blank cell and place it in the cell holder with the diamond mark facing you. Cover the cell compartment with the instrument cap to shield from stray light interferences and then press ZERO.
- (7) The instrument will turn on and the display will show --- then 0.00. Remove the blank cell and replace it with the prepared sample cell. Align the cell and cover the cell compartment and then press READ.
- (8) The instrument display will show --- followed by the results in ppm total chlorine. This is the total Cl₂ peroxygen value.

CALCULATION

$$\text{ppm H}_2\text{O}_2 = 0.478 \times (\text{total Cl}_2 \text{ peroxygen} - \text{total Cl}_2 \text{ PAA})$$