Method Validation Case Study: DPD Legacy Method Applied to Peracetic Acid

2019 NATIONAL ENVIRONMENTAL MONITORING CONFERENCE

Collaborative Efforts to Improve Environmental Monitoring

NEMC

Joanne Carpenter, CHEMetrics, Inc.
Harry McCarty, General Dynamics Information Technology

PAA BUZZ

From The Editor | November 19, 2014

EPA Investigates Chlorine Alternative

By Laura Martin
@LauraOnWater

In the U.S., chlorine has always been king when it comes to wastewater disinfection. But the EPA is investigating a "greener" alternative that could dethrone the chemical disinfectant. Peracetic acid (PAA) is gaining attention for its ability to reduce or eliminate disinfection byproducts (DBPs), sodium pollution, and total dissolved salts in treated water. It has been regularly used as a wastewater and stormwater disinfectant in Europe and Canada for the past 30 years, but only

Mechanism of Sporicidal Activity for the Synergistic Combination of Peracetic Acid and Hydrogen Peroxide

Mark J. Leggett[a], J. Spencer Schwarz[b], Peter A. Burke[c], Gerald McDonnell[c], Stephen P. Denyer[a] and Jean-Yves Maillard[a]

J. L. Schottel, Editor

+ Author Affiliations

- Author Affiliations

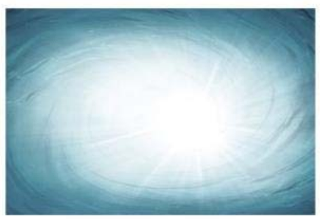
ABSTRACT

There is still great interest in controlling bacterial endospores. The use of chemical disinfectants and, notably, oxidizing agents to sterilize medical devices is increasing. Wi
until now there has been no explanation for the observed increase in sporicidal activity. This study provides information on the mechanism of synergistic interaction of PAA
combinations, including pretreatments with the two oxidizers, against wild-type spores and a range of spore mutants deficient in the spore coat or small acid-soluble spore
the assessment of any shift from H_2O_2 to PAA formation. This study confirmed the synergistic activity of the combination of H_2O_2 and PAA. However, we observed that
observed that the synergistic combination was based on H_2O_2 compromising the spore coat, which was the main spore resistance factor, likely allowing better penetration

The Age Of Peracetic Acid — A Solution To Increasingly Challenging Regulations

By Kati Bell and Varsha Wylie

While chlorination has long dominated water disinfection, new approaches and technologies have emerged in the wake of disinfection byproduct (DBP) regulations. Could peracetic acid (PAA) be the option that dethrones the king?



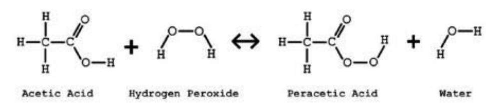
Chlorination became the standard for disinfecting treated wastewater in the 20th century and has been key to successfully protecting public health. However, awareness of environmental impacts associated with wastewater chlorination raised concerns regarding how to effectively balance destruction of pathogenic microorganisms against effects of disinfection byproducts (DBPs) that have both environmental and public health consequences. This issue

VigorOx® WWT II
Wastewater Disinfection Technology

Disinfection Forum
No 9, August 2015

VigorOx® WWT II Wastewater Disinfection Technology and Viruses

VigorOx® WWT II is an equilibrium peracetic acid solution that contains 15% peracetic acid (PAA) by weight at full concentration. The solution exists as an equilibrium of PAA, hydrogen peroxide, acetic acid and water as per:



Peracetic acid has been used as a low temperature biocide for
device disinfection and sterilization, food and food processing

Control Strategies for PAA Wastewater Disinfection at WWTPs with Variable Effluent Quality

Philip Block[1*], Scott Morgan[2], Kati Bell[3], Sarah Stewart[4]

[1]PeroxyChem, Philadelphia, PA
[2]City of Memphis, TN
[3]CDM Smith, Nashville, TN
[4]CDM Smith, Houston, TX

ABSTRACT

The dose of peracetic acid that is required to control microbial concentration in wastewaters will depend on a number of factors, including: target microorganism, the disinfection contact time, and the characteristic quality of the wastewater effluent. Wastewater characteristics that impact peracetic acid oxidant demand, and hence disinfection performance, may include natural

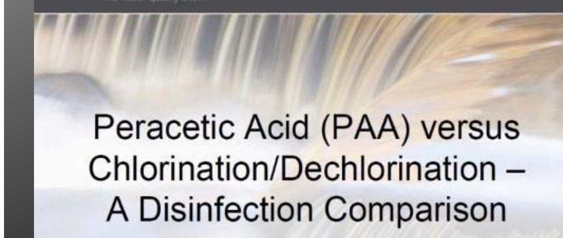
Peracetic Acid
A New Disinfection Approach

PNCWA 2009
September 15, 2008

Kelly Dancey, P.E.

CH2MHILL

weftec the water quality event® Technical Sessions



PAA COMPOSITION

Commercially available as an equilibrium mixture of:

- Peracetic acid 12-15%
- Hydrogen peroxide 18.5 – 23%
- Inert ingredients • acetic acid ~18% • water ~51%

$$CH_3CO_2H + H_2O_2 \rightleftharpoons CH_3CO_3H + H_2O$$

Acetic Acid **Hydrogen Peroxide** **PAA** **Water**

- PAA, Peroxyacetic Acid, Ethaneperoxoic acid, Peroxide of Acetic Acid

PAA Benefits Relative to Chlorine

- Replaces chlorine disinfection
- Broad spectrum of antimicrobial activity, (effective bactericide, fungicide, and sporicide)
- Fast disinfection kinetics
- Lower aquatic toxicity profile
- Decomposes to hydrogen peroxide (H_2O_2) and acetic acid which subsequently breaks down to oxygen and water
- Lack of disinfection by-product (DBPs) formation
- Oxidant demand typically lower than chlorine
- Does not persist in environment so quenching is not required
- Minimal pH dependence
- Long shelf-life
- Safe to store on-site

Source: PeroxyChem

WHY MONITOR PAA RESIDUAL?

1. Critical for the proper dosing of PAA to meet microbial reduction targets.

2. Monitoring is necessary to ensure regulatory water quality limits are being achieved, (typically around 1 ppm).

POTW OUTFALL

PRESENTATION OVERVIEW

PART 1

- Stakeholders
- What got the ball rolling?
- Standard Methods Organization
- Draft Method Process

PART 2

- Method Validation Planning\Process
- Group Testing
- Data Analysis

PRESENTATION OVERVIEW

PART 3

- Standard Methods Voting Process
- Standard Methods Publication

PART 4

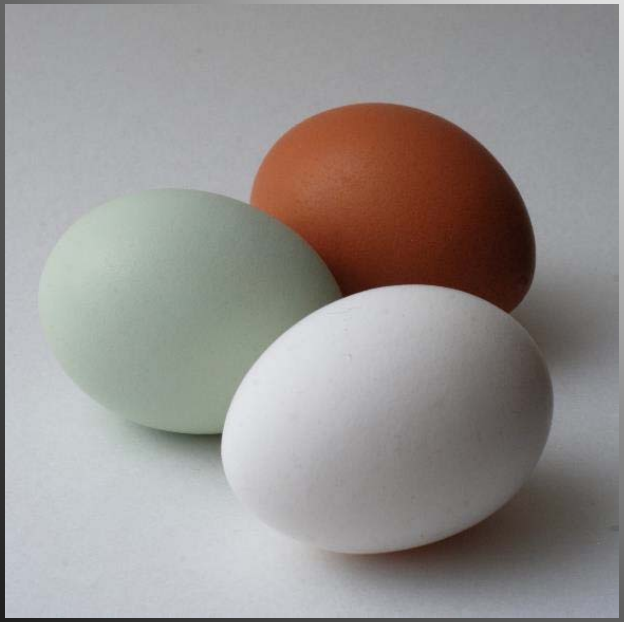
- EPA Review
- Initiate Method Promulgation Process\Sync with next Method Update Rule

PAA METHOD STAKEHOLDERS

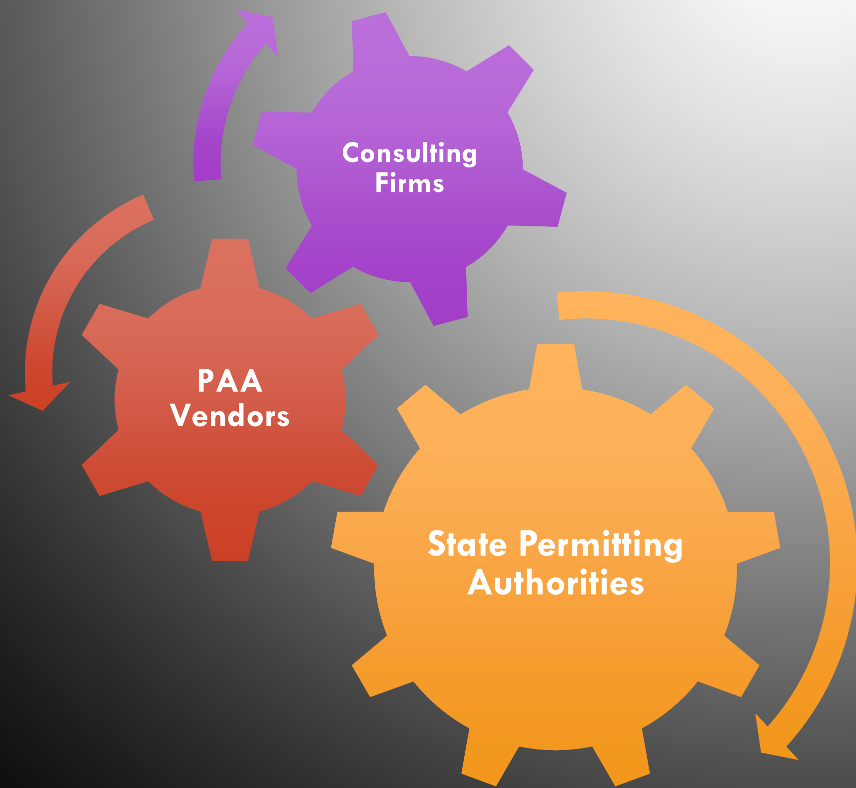
- POTW managers\engineers\operators
- EPA Office of Water\Office of Science and Technology\Engineering and Analysis Division
- State permitting authorities\agencies
- Engineering consulting firms
- PAA vendors
- Test kit vendors

WHICH COMES FIRST – THE CHICKEN OR THE EGG?

REGULATED PARAMETER OR APPROVED METHOD OF ANALYSIS?

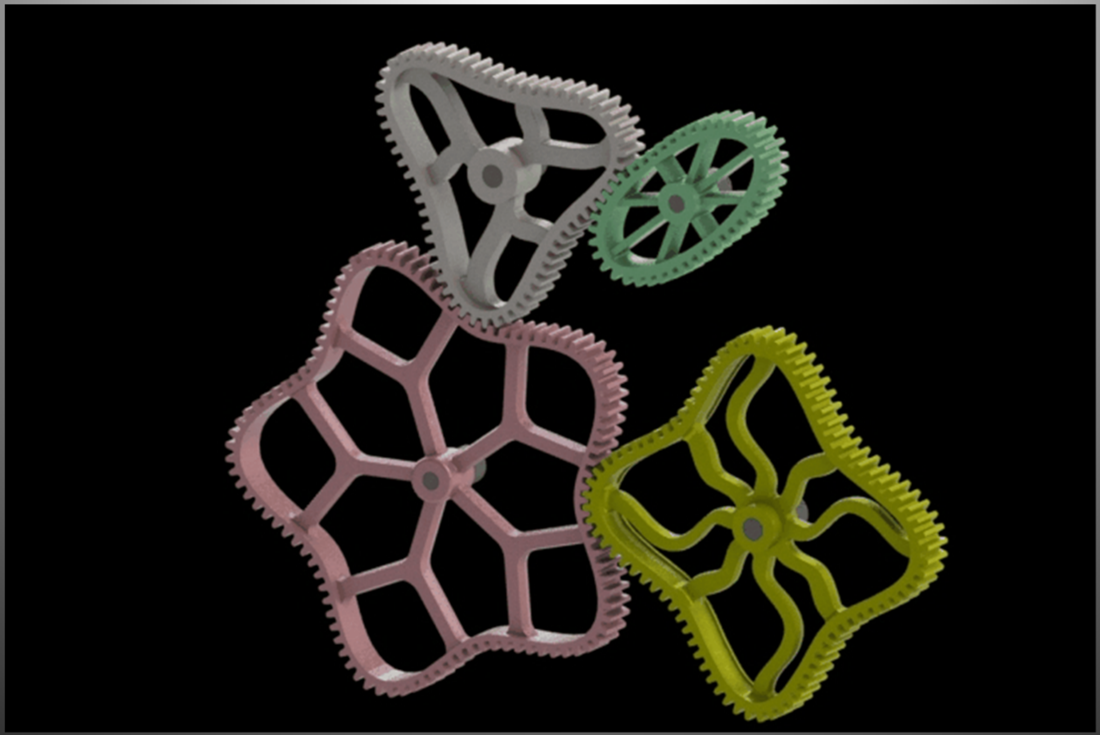


STATES' PERMITTING CHALLENGES



- How to establish limit for PAA residual with no Water Quality Standard?
- How to measure residual PAA with no approved method listed in 40 CFR 136?

Result?



PAA METHOD PUBLICATION\STANDARD METHODS IMPETUS

Water Environment Research Grant: LIFT14T16

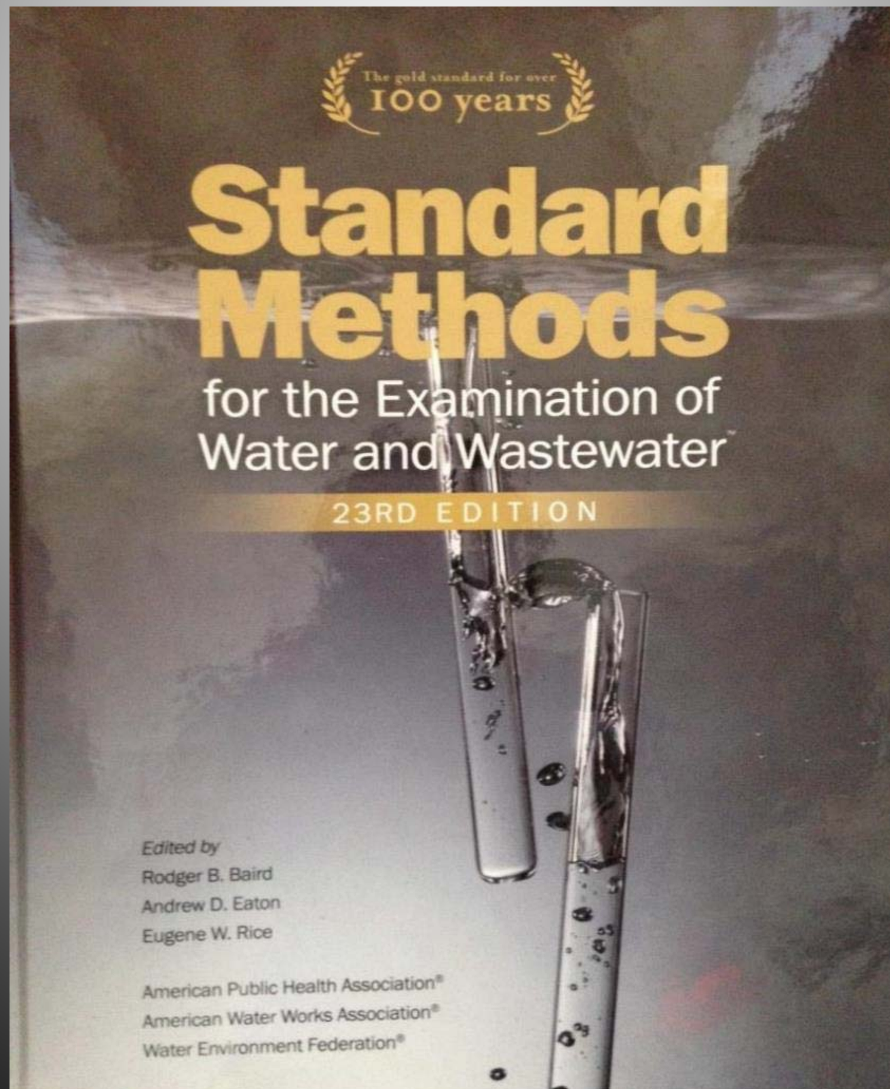
Evaluating Peracetic Acid as Disinfection Alternative in Wastewater Treatment Processes

- Publication of comprehensive guidance document that addresses specific research questions, documents current state of knowledge and identifies knowledge gaps
- LIFT14T16 awarded to Stantec in 2016

WATER ENVIRONMENT RESEARCH GRANT: LIFT14T16

(cont'd)

- What is PAA disinfection efficacy for:
  - Fecal and total coliforms
  - *E. coli* and Enterococcus
  - Bacteriophages and viruses
- How does wastewater quality impact PAA efficacy?
- How does PAA effect effluent pH, cBOD, COD, TOC, DO, and solids?
- What effect does PAA-treated effluent have on aquatic life?
- How else can PAA be used in wastewater treatment?
- What is needed to reduce regulatory ambiguity for PAA?


The gold standard for over
100 years
Standard Methods
for the Examination of Water and Wastewater™
23RD EDITION
Edited by
Rodger B. Baird
Andrew D. Eaton
Eugene W. Rice
American Public Health Association®
American Water Works Association®
Water Environment Federation®

STANDARD METHODS ORGANIZATION

- Joint Editorial Board (JEB)
- Part Coordinators
- Standard Methods Committee
- Joint Task Groups (JTG)

Joint Task Groups (JTGs) function as the primary working committees for review and revision of existing methods and development of new methods.

NEW OR REVISED METHOD?

The method is an adaptation or a modification of a current method	<u>Yes</u> No
The proposed method uses the same determination technique as the current method	<u>Yes</u> No
The proposed method maintains the same detector if an inorganic method.	<u>Yes</u> No
The proposed method has the same scope, an equivalent calibration range, and summary as the current method	<u>Yes</u> No
The proposed method maintains the sampling, preservation, or holding time requirements if compared to the current method	<u>Yes</u> No
The proposed method obtains equivalent or better results as the current method in samples that have no interferences	<u>Yes</u> No
The proposed method measures the same analyte, or chromophore if colorimetric, as the current method	Yes **<u>No</u>**

PAA Methods of Measurement

- DPD (N, N-diethyl-*p*-phenylenediamine) and potassium iodide
- Same colorimetric method used to measure total chlorine
- PAA is treated with an excess of potassium iodide and oxidizes it to iodine.
- Iodine subsequently oxidizes DPD to a pink color in direct proportion to the [PAA].
- Visual and instrumental PAA test kits are available.
- Pre-calibrated photometers are available.
- A blank measurement using a sample will help to reduce impact from wastewater background color, turbidity or other constituents.

DPD METHOD – LONG HAND VS. TEST KIT

FROM SCRATCH

- DPD
- Phosphate buffer
- EDTA
- Potassium iodide

TEST KIT (ALL INCLUSIVE REAGENT) WITH PRE-CALIBRATED PHOTOMETER

- Foil pack
- Ampoule

WRITING METHOD 2017-2018

“SINGLE OPERATOR”
COMBINED TEST KIT DATA
PERFORMANCE CHARACTERISTICS

- MDL: ~ 0.07 ppm
- ML: ~ 0.15 ppm
- Initial Demonstration of Capability % recovery limits (based on 20 replicates): 87 – 111%

FINISHED PRODUCT

4500-PAA PERACETIC ACID (RESIDUAL) (PROPOSED)

4500-PAA A. Introduction

1. Peracetic Acid as a Wastewater Disinfectant

While U.S. municipal treatment plants still commonly use chlorination to disinfect wastewater, concerns about chlorinated disinfection byproducts (DBPs) are prompting utilities to consider other disinfection technologies. One alternative is peracetic acid (PAA), which does not form chlorinated DBPs.[1]

PAA's effectiveness as a disinfectant depends on its dose, contact time, and the target organisms' susceptibilities. Its oxidant demand in wastewater depends on the wastewater's characteristics (e.g., natural organic matter, reduced metals, biological oxygen demand, chemical oxygen demand, and total suspended solids).

METHOD VALIDATION [COLLABORATIVE STUDY] DESIGN REFERENCES

- Standard Methods *Section 1040 C. Collaborative Testing*
- ASTM D2777-13 *Standard Practice for Determination of Precision and Bias of Applicable Test Methods*
- ASTM E691-18 *Standard Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method*
- EPA's "*Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program*

PAA DEMAND CHALLENGES IMPACTS ON STUDY DESIGN

- Spiking and distributing samples
- Replicate analysis
- Analysis start time

DETERMINING METHOD PRECISION AND BIAS STATEMENTS

Youden Pair Graphical Method

- Embraced by consensus organizations
- Youden pairs enable the calculation of single operator, multiple operator (overall) precision and % recovery per matrix
- Lends itself to situations where analyte is labile
- Two spike aliquots from the same matrix are prepared.
- The spike concentration for each aliquot differ only by 5 – 20% in concentration.
- Each laboratory runs each sample only once.

DETERMINING METHOD PRECISION AND BIAS STATEMENTS

Youden Pair Graphical Method, cont'd

- The scatter plots derived from the compiled lab test results for each matrix will reveal:
  - If labs are equivalent
  - Which particular labs are outliers
  - Distinguish random from systematic errors

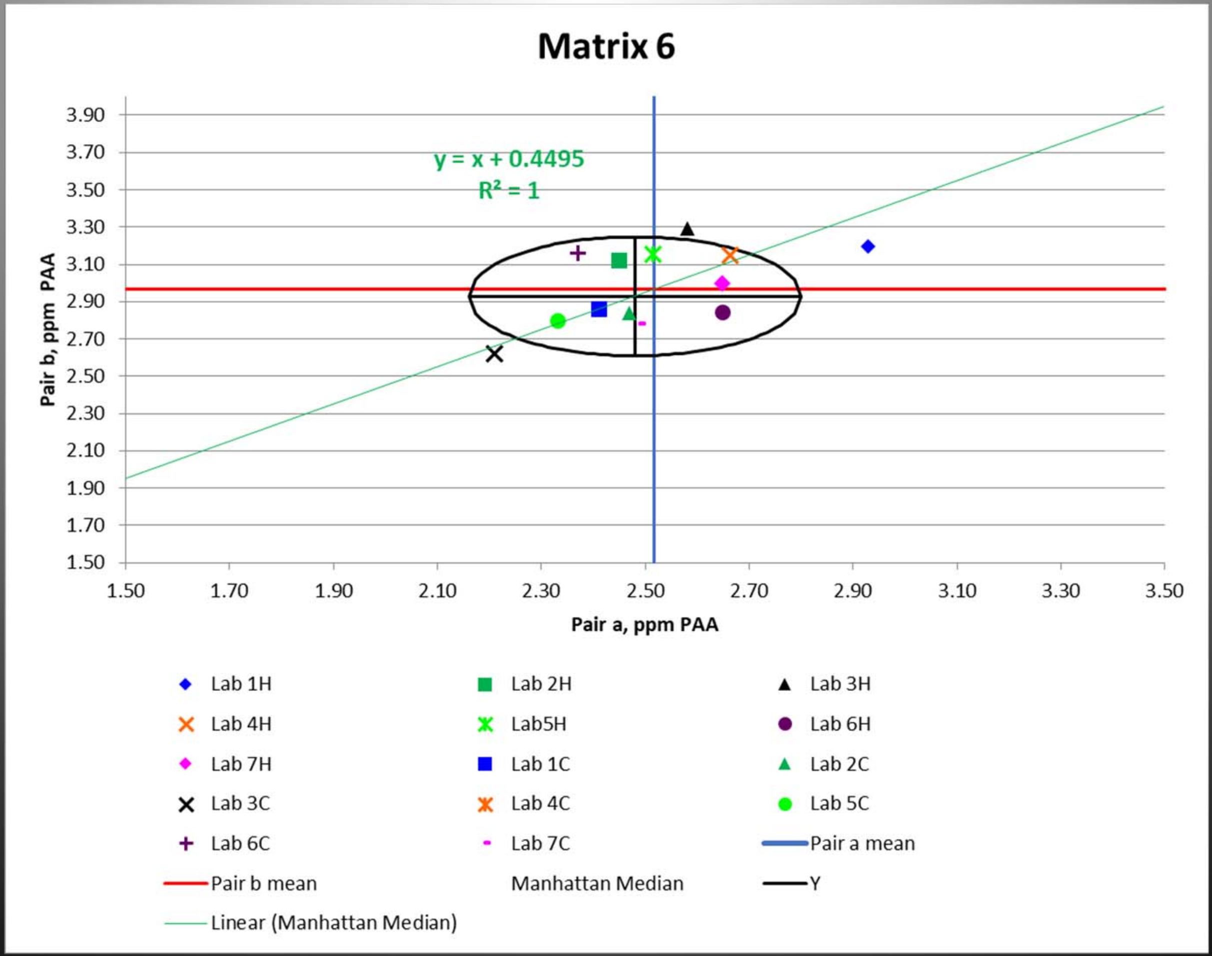
VALIDATION PROTOCOL

- 7 labs, (analysts)
- Two PAA test kits\photometers (2 vendors)
- 9 final effluent wastewater matrices
- 7 x 2 = 14 data points\matrix

ONE LOCATION

"LABS"\ANALYSTS

VALIDATION DATA – FOCUS ON ONE MATRIX



VALIDATION SUMMARY DATA – ALL MATRICES
SINGLE OPERATOR STATS

Statistic	Matrix 1	Matrix 2	Matrix 3	Matrix 4	Matrix 5	Matrix 6	Matrix 7	Matrix 8	Matrix 9
# of useable pairs	13	13	13	14	14	13	12	13	14
Average Concentration	0.36	0.85	1.27	1.94	2.44	2.75	3.69	4.03	3.28
Single Operator Standard Deviation, S_o	0.037	0.053	0.050	0.069	0.061	0.130	0.095	0.140	0.194
Single Operator Relative Standard Deviation, %	10.4	6.23	3.93	3.56	2.50	4.74	2.58	3.47	5.92

VALIDATION SUMMARY DATA – MATRICES 1-5 MULTIPLE OPERATOR STATS

Matrix ID #	Pair ID	Number of useable values	Target Dose Value, ppm PAA	Actual Dose Value, ppm PAA	Grand Average Concentration	% recovery relative to target dose	% recovery relative to actual dose	Multiple lab Standard Deviation (St)	Overall % RSD
1	Pair a	13	0.30	0.33	0.32	105	96	0.090	28.6
1	Pair b	14	0.36	0.40	0.39	109	98	0.068	17.3
2	Pair a	13	0.70	0.84	0.73	104	87	0.062	8.48
2	Pair b	14	0.84	1.01	0.95	114	94	0.113	11.9
3	Pair a	13	1.10	1.37	1.07	97	78	0.088	8.17
3	Pair b	13	1.32	1.65	1.35	102	82	0.070	5.17
4	Pair a	13	1.60	1.92	1.82	114	95	0.116	6.35
4	Pair b	12	1.92	2.31	2.06	107	89	0.043	2.08
5	Pair a	13	2.10	2.52	2.26	108	90	0.103	4.55
5	Pair b	14	2.52	3.02	2.63	104	87	0.062	2.34

VALIDATION SUMMARY DATA – MATRICES 6 - 10 MULTIPLE OPERATOR STATS

Matrix ID #	Pair ID	Number of useable values	Target Dose Value, ppm PAA	Actual Dose Value, ppm PAA	Grand Average Concentration	% recovery relative to target dose	% recovery relative to actual dose	Multiple lab Standard Deviation (St)	Overall % RSD
6	Pair a	13	2.50	3.20	2.52	101	79	0.183	7.26
6	Pair b	14	3.00	3.80	2.97	99	78	0.211	7.12
7	Pair a	14	3.10	4.03	3.38	109	84	0.074	2.19
7	Pair b	14	3.72	4.84	4.00	108	83	0.135	3.37
8	Pair a	14	4.00	4.95	3.75	94	76	0.292	7.79
8	Pair b	14	4.80	5.80	4.31	90	74	0.339	7.85
9	Pair a	14	4.10	5.74	2.96	72	52	0.373	12.6
9	Pair b	14	4.92	6.88	3.60	73	52	0.549	15.2

STANDARDMETHODS

PeroxyChem

Certificate of Completion

THIS ACKNOWLEDGES THAT

Joanne Carpenter

HAS SUCCESSFULLY COMPLETED THE

PERACETIC ACID PALOOZA

JULY 17 – 19, 2018

TONAWANDA, NEW YORK

AND IS CERTIFIED AS A

POUCH POOCHER

CHEMetrics

HACH

STANDARD METHODS VOTING PROCESS

1. Prepare a Validation Report
2. Balloted at JTG level
3. Negative ballots and JTG comments are reviewed by JEB, the PC and the JTG Chair for resolution (negatives) or consideration for inclusion in the section (comments).
4. Balloted at Main Committee level

STANDARD METHODS BALLOTING PROCESS
METHOD CLASSES

- PROPOSED – method has not yet undergone the method validation requirements
- STANDARD – method has either:
  - Undergone development, validation and collaborative testing requirements
  - "WIDELY USED"
- Print edition published about every 5 years
- On-line edition – users will have access to the most current methods available

EPA NEW METHOD REVIEW PROCESS

- Follow Guidelines published EPA's "*Protocol for Review and Validation of New Methods for Regulated Organic and Inorganic Analytes in Wastewater Under EPA's Alternate Test Procedure Program* to evaluate data and prepare report in EPA format.

https://www.epa.gov/sites/production/files/2018-03/documents/chemical-new-method-protocol_feb-2018.pdf

EPA NEW METHOD REVIEW PROCESS

- Method Update Rules (MURs)
- EPA compiles the rule docket (~ minimum 9 month process)
- Public comment period
- Public comment aftermath
- Final rule

PAA DPD METHOD CURRENT STATUS

- Standard Methods balloting

FOCUS ON ONE MATRIX
SINGLE OPERATOR STANDARD DEVIATION

Matrix 6 Single Operator Standard Deviation, S_0							
Lab ID Code	Pair a	Pair b	(Di)	(Di - Dbar)2	sum(Di - Dbar)2	sum(Di - Dbar)/(2(m-1))	sum(Di - Dbar)/(2(m-1))1/2 Single Operator Standard Deviation, S0
1	2.93	3.20	0.27	0.041	0.41	0.017	**0.130**
2	2.45	3.12	0.67	0.041		m = 13	
3	2.58	3.30	0.71	0.060			
4	2.66	3.15	0.48	0.000			
5	2.51	3.15	0.64	0.029			
6	2.65	2.85	0.20	0.073			
7	2.65	3.00	0.35	0.015			
8	2.41	2.86	0.45	0.000			
9	2.47	2.84	0.37	0.010			
10	2.21	2.62	0.41	0.004			
11							
12	2.33	2.80	0.47	0.000			
13	2.37	3.16	0.79	0.103			
14	2.49	2.78	0.29	0.032			
Mean	**2.75**		**0.47**				
% RSD	**4.7**						

FOCUS ON ONE MATRIX
MULTIPLE LAB STANDARD DEVIATION

Matrix 6 Multiple Operator Standard Deviation, S_t											
Lab ID Code	Pair a	(xi - xbar)2	sum(xi - xbar)2	sum(xi - xbar)2/(n-1)	[sum(xi - xbar)2/(n-1)]1/2 Multiple Lab Standard Deviation, St	Pair b	(xi - xbar)2	sum(xi - xbar)2	sum(xi - xbar)2/(n-1)	[sum(xi - xbar)2/(n-1)]1/2 Multiple Lab Standard Deviation, St
1	2.93	0.171	0.400	0.033	0.183	3.20	0.053	0.580	0.045	**0.211**
2	2.45	0.005		n = 13		3.12	0.024		n = 14	
3	2.58	0.004				3.30	0.108			
4	2.66	0.022				3.15	0.032			
5	2.51	0.000				3.15	0.035			
6	2.65	0.017				2.85	0.014			
7	2.65	0.017				3.00	0.001			
8	2.41	0.011				2.86	0.011			
9	2.47	0.002				2.84	0.016			
10	2.21	0.094				2.62	0.120			
11						2.71	0.066			
12	2.33	0.035				2.80	0.028			
13	2.37	0.021				3.16	0.038			
14	2.49	0.001				2.78	0.035			
Mean	**2.52**				**Mean**	**2.97**				
% RSD	**7.3**				**% RSD**	**7.1**				