Subject:	Online TRO Analyzer Evaluation and Benchmark Study
Date:	June 9, 2020
By:	Kent D. Henry, *Ph.D.*

OVERVIEW

The objective of this evaluation is to assess the performance of the current state of online TRO analyzers in a simulation of ballast water tank chlorination, hold, and dechlorination. The analyzer performance is compared to TRO results acquired from grab samples evaluated with a Hach Pocket Colorimeter II.

The test plan was prepared and supervised by Dr. Kent D. Henry.

EXECUTIVE SUMMARY

The purpose of the evaluation is to compare current and new DPD-based and amperometric-based analyzers in environments simulating in-tank ballast water treatment operations across salinities of fresh, brackish, and seawater. The evaluation is benchmarked against grab samples measured using a Hach Pocket Colorimeter II.

There are application-driven needs related to analyzer installation and operation that greatly impact the overall cost of ownership and user satisfaction. To this need, DPD and amperometric TRO analyzers provide different opportunities. Therefore, another purpose of the evaluation is to ascertain the state of the art in on-line TRO analyzer performance and determine if there are viable new developments for the ballast water treatment industry.

This benchmark study reveals that the evaluated TRO analyzers are generally statistically indistinguishable in their performance. The DPD and amperometric analyzers as a group performed statistically the same when benchmarked to grab samples analyzed using a Hach Pocket Colorimeter II.

Contents

TEST PLAN AND EXPERIMENTAL

EQUIPMENT

TRO Analyzers that completed the evaluation

1. HF Scientific, CLX-XT, Ballast Water TRO Analyzer, DPD Based (new, factory calibrated, out-of-the-box)
2. HF Scientific, CLX-EX, Ballast Water TRO Analyzer, DPD Based (new, factory calibrated, out-of-the-box)
3. HF Scientific, SSR, Ballast Water TRO Analyzer, DPD Based (new, factory calibrated, out-of-the-box)
4. Lucent Water, TRO Analyzer, Solid-State Based (new, factory calibrated, out-of-the-box)
5. Lucent Water, TRO Analyzer, Solid-State Based (new, factory calibrated, out-of-the-box)

TRO Analyzers that failed during the pre-evaluation

6. OI Analytical, Ballast Water TRO Analyzer, DPD Based (new 11/2018, ran fine during 2018 evaluation and for several months during pre-evaluations, failed when the final experimental setup was completed for this evaluation)
7. HalogenSys, SWN-P, TRO Analyzer, Solid-State Based (new 2/2019, failed during pre-evaluation)
8. HalogenSys, EX-P-STD, TRO Analyzer, Solid-State Based (new 2/2019, did not function during the pre-evaluation)

General Equipment

- Surrogate ballast tank - 2.37 m^3 (625 gallons), tank filled to 1.89 m^3 (500 gallons)
- Ballast mixing/circulation pump – Warrender MT5003 operating at ~5.0 m^3/h (22 GPM); tank exchange in 22.7 minutes
  Single GPI TM100-N digital flow meter
- Sample line pump - March 335 operating at ~1.8 m^3/h (8.0 GPM); tank exchange in 62.5 minutes
  Dual GPI TM075-N digital flow meters
- Circulation Hoses – DN38 (1-1/2”) hoses of various lengths
- Sample Tubes – 6 mm (1/4”) tubing < 2 m to each DPD TRO Analyzer
- Hach Pocket Colorimeter II, Total Chlorine
- Apera Model PC60 for pH
- YSI Model Pro1030 water quality meter for salinity/conductivity/temperature
- Instant Ocean sea salt

Programmable NaOCl / Na_2SO_4 dosing system

- Bleach, 6.26% Sodium Hypochlorite; Great Value brand
- Dechlor, Sodium Sulfate; Chem Out brand
  - Solution: mixed 50 grams dechlor dissolved in 1000 mL DI water
- Dosed every 90 minutes
  - Two peristaltic pumps (1 bleach; 1 dechlor solution)
  - Programmable dosing system (Microcontroller)
  - Clearflex Premium PVC tubing

Grab sample measurements

- Hach Pocket Colorimeter II
  - Total Chlorine Swiftest
  - Free Chlorine Swiftest
- Four 10-mL glass sample cells with caps
- 50-mL glass volumetric flask with stopper
- 5-mL Pipette with pipette headers
- Two sets of Hach Calibration vials P/N 2635300
- Precision fill bottle with DI water
- Kimtech Kimwipes
- Rinse bottle with DI water
- Sample container

EXPERIMENTAL SETUP

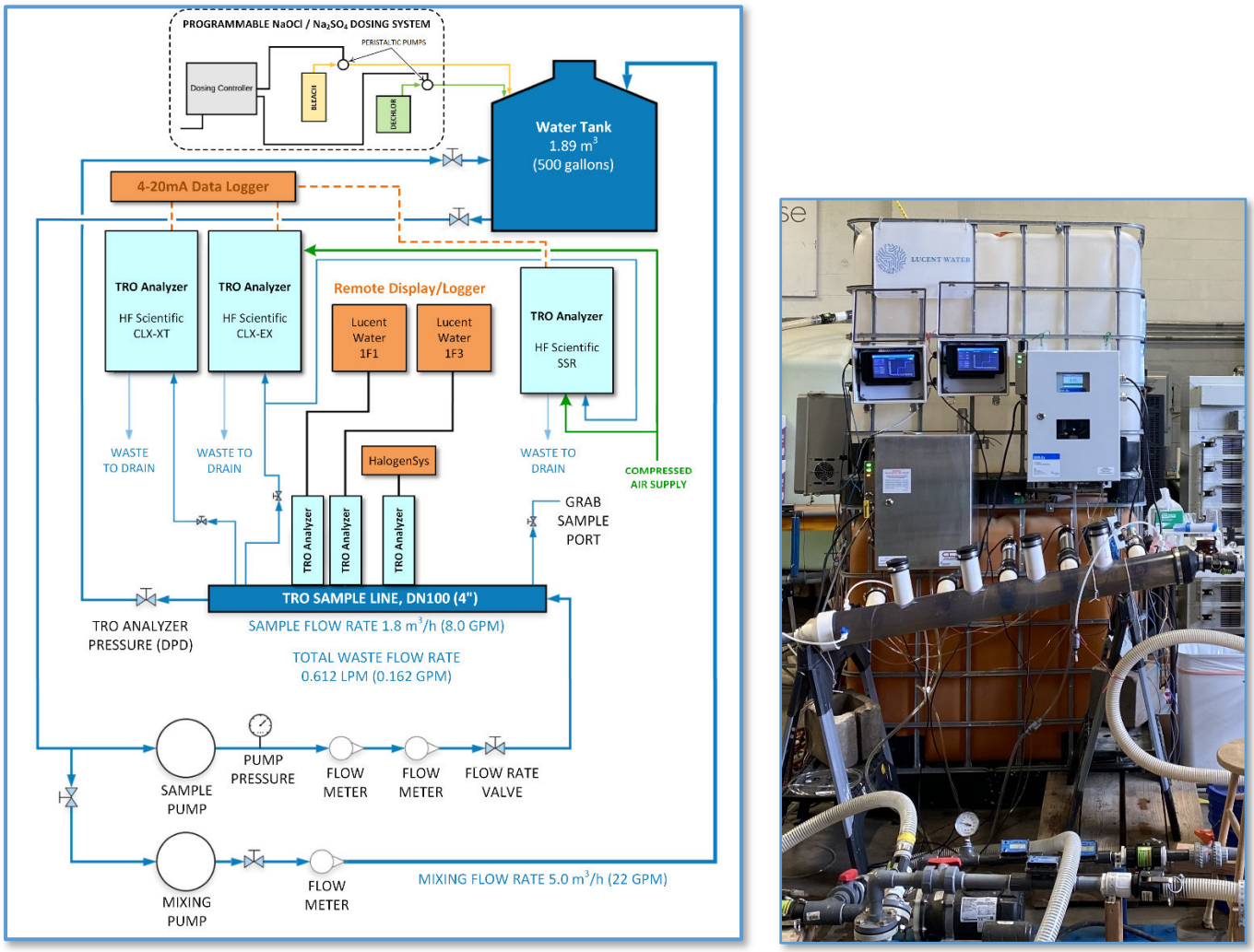


Figure 1: Experimental setup block diagram (left) and actual setup (right).

Figure 2: Analyzers 1 through 7 in the equipment list are shown.

EXPERIMENTAL

TRO ANALYZERS

- Each analyzer was operated out-of-the-box.
- Data from the DPD analyzers were recorded using a 4-20mA data logger
    - HF Scientific, CLX-XT 60-second cycle time, with averages set to 1 (no averaging, real-time data)
    - HF Scientific, CLX-EX 60-second cycle time, with averages set to 1 (no averaging, real-time data)
    - HF Scientific, SSR 180-second cycle time, with averages set to 2 (average of current and prior value)
- Data from the amperometric analyzers were recorded from their on-board data memory
    - Lucent Water, TRO Analyzers 90-second cycle time, with averages set to 5 (average of current with four prior values)
- Sample line pressure was adjusted to facilitate the requirements of the DPD-analyzers. The pressure was not recorded.
- Planned to record nine (9) TRO setpoints: 0, 2.5, 5.0, 6.5, 9.0, 7.0, 3.0, 1.0, and 0 ppm. The actual values and whether all nine setpoints were achieved varied.
- Each TRO setpoint was dwelled for 90 minutes.
- Grab samples were recorded at 30 and 75 minutes after the setpoint was adjusted.
- The experiment measured TRO in three (3) water salinities: seawater, brackish, and fresh

GRAB SAMPLES

1. Collect grab sample from the indicated port
    a. Take an aliquot
    b. Rinse the sample cup
    c. Dispose of the aliquot
    d. Repeat aliquot two more times
    e. Collect the sample

2. Prepare a sample dilution based on the estimated tank TRO and 2.0 ppm as the upper limit for the Hach Pocket Colorimeter II. This is the amount of sample to dilute to 50 mL using the volumetric flask.
    a. Based on equation $C_1V_1 = C_2V_2$
    b. 10 mL for 5-10 ppm range (reading expected to be 1.0 to 2.0 ppm)
    c. 20 mL for 2-5 ppm range (reading expected to be 0.8 to 2.0 ppm)
    d. No dilution for 0-2 ppm range
3. Pipette sample into 50-mL volumetric flask
    a. Set pipette volume
    b. Withdraw and dispose sample three times
    c. Withdraw and inject sample into volumetric flask
4. Fill remainder of volumetric flask with DI water
    a. Use precision fill bottle
    b. Fill to the 50-mL mark
5. Mix volumetric flask
    a. Place glass stopper onto the volumetric flask
    b. Invert the volumetric flask 5-10 times
6. Rinse each of four colorimeter sample cells
    a. Add an aliquot to the sample cell
    b. Swill the sample cell
    c. Dispose of the aliquot
    d. Repeat a single time for each sample cell
7. Fill each of four sample cells
    a. Use diluted mixture from volumetric flask
    b. Fill each sample cell to approximately the 10mL indicator line
8. Zero the colorimeter
    a. Use a Kimwipe to remove smudges on the sample cell
    b. Make sure that the sample is clear without particulates and bubbles
    c. Place one sample cell at random into the colorimeter
    d. Zero the colorimeter
9. Add Total Chlorine DPD reagent to each of four sample cells
    a. Add the total powder to each sample cell
    b. Start count-down timer for 3 minutes
    c. Invert all capped cells ~3 times smoothly in the first 60 seconds
10. Read and record TRO values
    a. Use Kimwipes to remove smudges on the sample cells
    b. Measure and record the TRO value for each sample
    c. Record the scientific average for all four reading
    d. Convert the average TRO value using $C_1V_1 = C_2V_2$
11. Rinse each sample cell and volumetric flask
    a. Use DI water
    b. Add an aliquot of DI water to each cell and flask
    c. Swirl to coat all surfaces
    d. Discard the aliquot
    e. Repeat three times
    f. Rinse sample cell caps under a stream of DI water
    g. Set aside to drain until next use
12. Repeat process for Free Chlorine using same sample collected in step 1.

RESULTS

EXPERIMENT DAYS

The evaluation took place over seven (7) days as follows:

Day 0 – April 28: Equipment setup

Day 1 – April 29: System adjustments to achieve tank mixing, sample line flow, sample line back pressure

Day 2 – April 30: Seawater evaluation began but additional adjustments were required to the experimental apparatus

Day 3 – May 1: Seawater evaluation began but additional training was necessary for the personnel monitoring the equipment and performing the grab samples analyses

Day 4 – May 2: Seawater evaluation

Day 5 – May 3: Idle day. DPD analyzers off; amperometric analyzers on; mixing pump off; sample pump on with neutralized seawater from the prior day

Day 6 – May 4: Brackish water evaluation

Day 7 – May 5: Fresh water evaluation

Day 8 – May 6: Equipment disassembled

WATER CONDITIONS

Table 1: Surrogate ballast water conditions

Water Condition	Conductivity (µS/cm)	Salinity (ppt)	pH	Temperature (°C)
Seawater	47,190	33.4	8.15	21.2
Brackish water	17,310	11.9	8.22	18.2
Fresh water	339	0.2	8.03	16.2

Notes:

1. The ballast water tank was filled and salinity adjusted the night before each experiment. The tank circulated overnight using the sample pump.
2. The incoming freshwater was not softened prior to use
3. The fresh water supply temperature is typically below 12 °C

DATA ANALYSIS

The data acquired from each TRO analyzer and the grab samples was presented over time without any adjustment.

The data recording for each sensor is as follows:

Data from the DPD analyzers were recorded using a 4-20mA data logger

- HF Scientific, CLX-XT 60-second cycle time, with averages set to 1 (no averaging, real-time data)
- HF Scientific, CLX-EX 60-second cycle time, with averages set to 1 (no averaging, real-time data)
- HF Scientific, SSR 180-second cycle time, with averages set to 2 (average of current and prior value)

Data from the amperometric analyzers were recorded from their on-board data memory

- Lucent Water, TRO Analyzers 90-second cycle time, with averages set to 5 (average of current with four prior values)

Seawater results: Figure 3 on page 7 and Table 2 on page 8

Brackish water results: Figure 4 on page 9 and Table 3 on page 10

Fresh water results: Figure 5 on page 11 and Table 4 on page 12

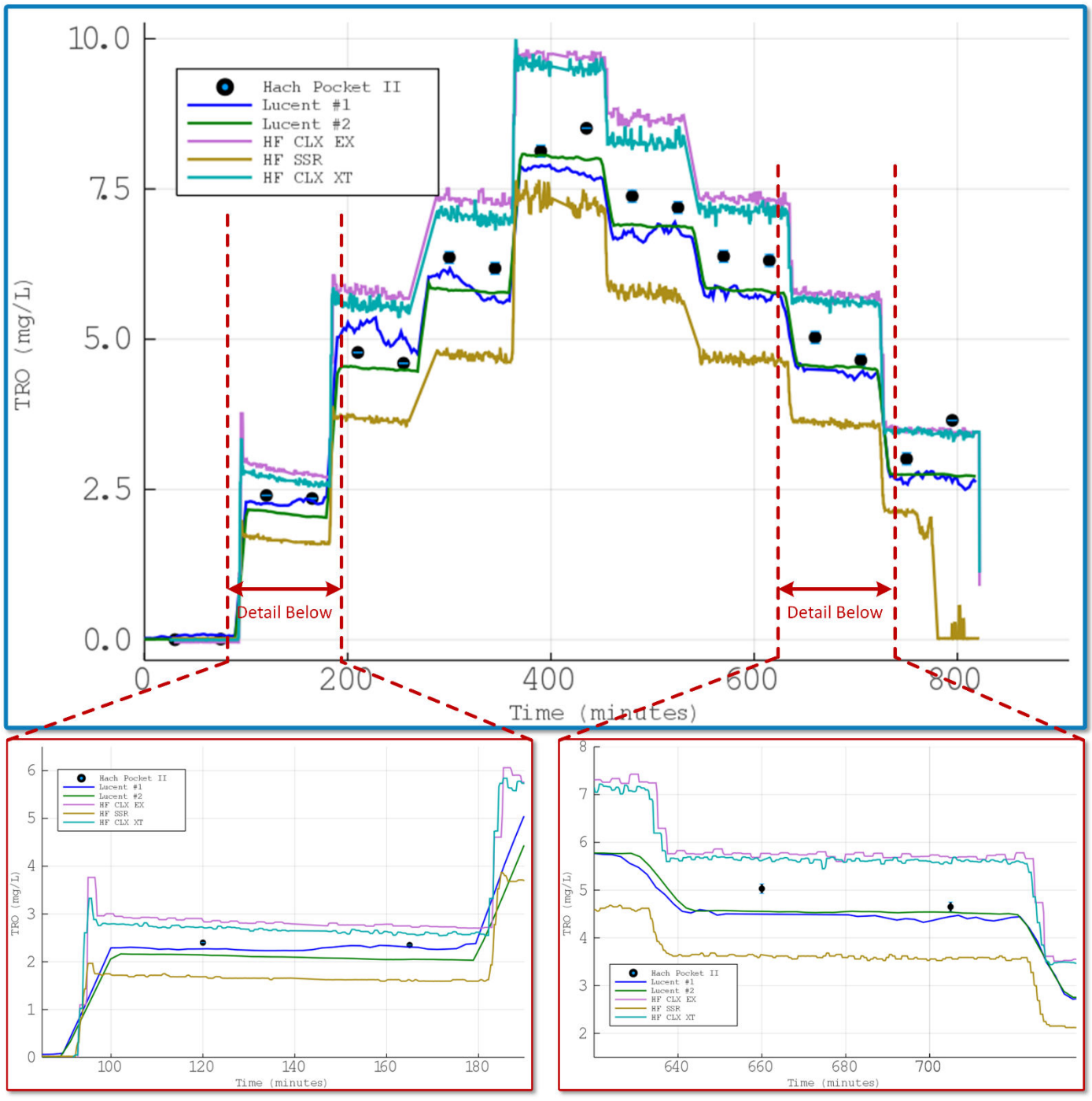


Figure 3: Data from seawater, as recorded

Table 2: TRO Results – **Seawater** (see **TRO RESULTS TABLE N** on page 13)

Original Data, Out-of-the-Box Operation

			Seawater				
Water Condition	**TOTAL Cl_2**	**FREE Cl_2**	**HF SSR**	**HF XT**	**HF EX**	**LW 1**	**LW 3**
Grab Sample 1, ppm	0.00	0.02	0.02	-0.01	-0.04	0.04	0.01
Grab Sample 2, ppm	0.01	0.01	0.02	0.00	-0.04	0.08	0.01
Error (pppm)			0.01	-0.01	-0.04	0.05	0.00
Grab Sample 3, ppm	2.40	2.02	1.69	2.71	2.84	2.27	2.15
Grab Sample 4, ppm	2.35	2.01	1.60	2.58	2.73	2.32	2.05
Error (pppm)	Free 85% of Total		-0.73	0.27	0.41	-0.08	-0.28
Grab Sample 5, ppm	4.78	4.44	3.68	5.54	5.83	5.12	4.54
Grab Sample 6, ppm	4.60	4.37	3.65	5.51	5.67	5.12	4.49
Error (pppm)	Free 94% of Total		-1.02	0.84	1.06	0.43	-0.17
Grab Sample 7, ppm	6.36	5.57	4.72	7.04	7.32	6.09	5.83
Grab Sample 8, ppm	6.18	5.47	4.68	6.83	7.24	5.70	5.76
Error (pppm)	Free 88% of Total		-1.57	0.67	1.01	-0.37	-0.47
Grab Sample 9, ppm	8.13	7.66	7.25	9.54	9.77	7.87	8.06
Grab Sample 10, ppm	8.51	7.35	7.16	9.49	9.69	7.76	7.98
Error (pppm)	Free 90% of Total		-1.12	1.19	1.41	-0.51	-0.30
Grab Sample 11, ppm	7.38	6.32	5.90	8.23	8.68	6.78	6.90
Grab Sample 12, ppm	7.19	6.45	5.74	8.44	8.67	6.95	6.88
Error (pppm)	Free 88% of Total		-1.46	1.05	1.39	-0.42	-0.40
Grab Sample 13, ppm	6.38	5.58	4.65	7.19	7.38	5.80	5.86
Grab Sample 14, ppm	6.31	5.45	4.65	6.93	7.31	5.63	5.80
Error (pppm)	Free 87% of Total		-1.69	0.72	1.00	-0.63	-0.51
Grab Sample 15, ppm	5.03	4.29	---	---	---	4.50	4.56
Grab Sample 16, ppm	4.65	3.31	3.56	5.65	5.68	4.41	4.54
Error (pppm)	Free 79% of Total		-1.28	0.82	0.84	-0.38	-0.29
Grab Sample 17, ppm	3.01	2.71	2.15	3.50	3.50	2.60	2.75
Grab Sample 19, ppm	3.65	2.58	---	3.39	3.45	2.71	2.74
Error (pppm)	Free 79% of Total		-1.18	0.11	0.14	-0.68	-0.59
Per Experiment Error			**-1.12**	**0.63**	**0.80**	**-0.29**	**-0.33**
Per Experiment Sdev			**0.52**	**0.42**	**0.52**	**0.36**	**0.18**
Error - / + Sdev			-1.63 to -0.60	0.21 to 1.04	0.28 to 1.32	-0.65 to 0.07	-0.52 to -0.15

One-Point Span Corrected to Measurements at Brackish 6 ppm

			Seawater				
Water Condition	**TOTAL Cl_2**	**FREE Cl_2**	**HF SSR**	**HF XT**	**HF EX**	**LW 1**	**LW 3**
Grab Sample 1, ppm	0.00	0.02	0.02	-0.01	-0.03	0.03	0.01
Grab Sample 2, ppm	0.01	0.01	0.03	0.00	-0.03	0.07	0.01
Error (pppm)			0.02	-0.01	-0.04	0.04	0.00
Grab Sample 3, ppm	2.40	2.02	2.14	2.21	2.32	1.93	2.03
Grab Sample 4, ppm	2.35	2.01	2.02	2.10	2.23	1.98	1.94
Error (pppm)	Free 85% of Total		-0.29	-0.22	-0.10	-0.42	-0.39
Grab Sample 5, ppm	4.78	4.44	4.67	4.52	4.78	4.36	4.29
Grab Sample 6, ppm	4.60	4.37	4.63	4.49	4.65	4.36	4.25
Error (pppm)	Free 94% of Total		-0.04	-0.18	0.02	-0.32	-0.42
Grab Sample 7, ppm	6.36	5.57	5.98	5.74	6.00	5.19	5.51
Grab Sample 8, ppm	6.18	5.47	5.94	5.57	5.94	4.86	5.45
Error (pppm)	Free 88% of Total		-0.31	-0.61	-0.30	-1.24	-0.79
Grab Sample 9, ppm	8.13	7.66	9.20	7.78	8.01	6.71	7.62
Grab Sample 10, ppm	8.51	7.35	9.08	7.74	7.95	6.61	7.55
Error (pppm)	Free 90% of Total		0.82	-0.56	-0.35	-1.66	-0.74
Grab Sample 11, ppm	7.38	6.32	7.48	6.71	7.12	5.78	6.52
Grab Sample 12, ppm	7.19	6.45	7.28	6.88	7.11	5.92	6.51
Error (pppm)	Free 88% of Total		0.10	-0.49	-0.17	-1.43	-0.77
Grab Sample 13, ppm	6.38	5.58	5.90	5.86	6.05	4.94	5.54
Grab Sample 14, ppm	6.31	5.45	5.90	5.65	5.99	4.80	5.48
Error (pppm)	Free 87% of Total		-0.44	-0.58	-0.32	-1.47	-0.83
Grab Sample 15, ppm	5.03	4.29	---	---	---	3.84	4.31
Grab Sample 16, ppm	4.65	3.31	4.51	4.61	4.66	3.76	4.29
Error (pppm)	Free 79% of Total		-0.33	-0.23	-0.18	-1.04	-0.54
Grab Sample 17, ppm	3.01	2.71	2.73	2.85	2.87	2.22	2.60
Grab Sample 19, ppm	3.65	2.58	---	2.77	2.82	2.31	2.59
Error (pppm)	Free 79% of Total		-0.60	-0.52	-0.49	-1.07	-0.74
Per Experiment Error			**-0.12**	**-0.38**	**-0.21**	**-0.96**	**-0.58**
Per Experiment Sdev			**0.42**	**0.22**	**0.16**	**0.59**	**0.27**
Error - / + Sdev			-0.54 to 0.30	-0.60 to -0.16	-0.38 to -0.05	-1.55 to -0.37	-0.85 to -0.31

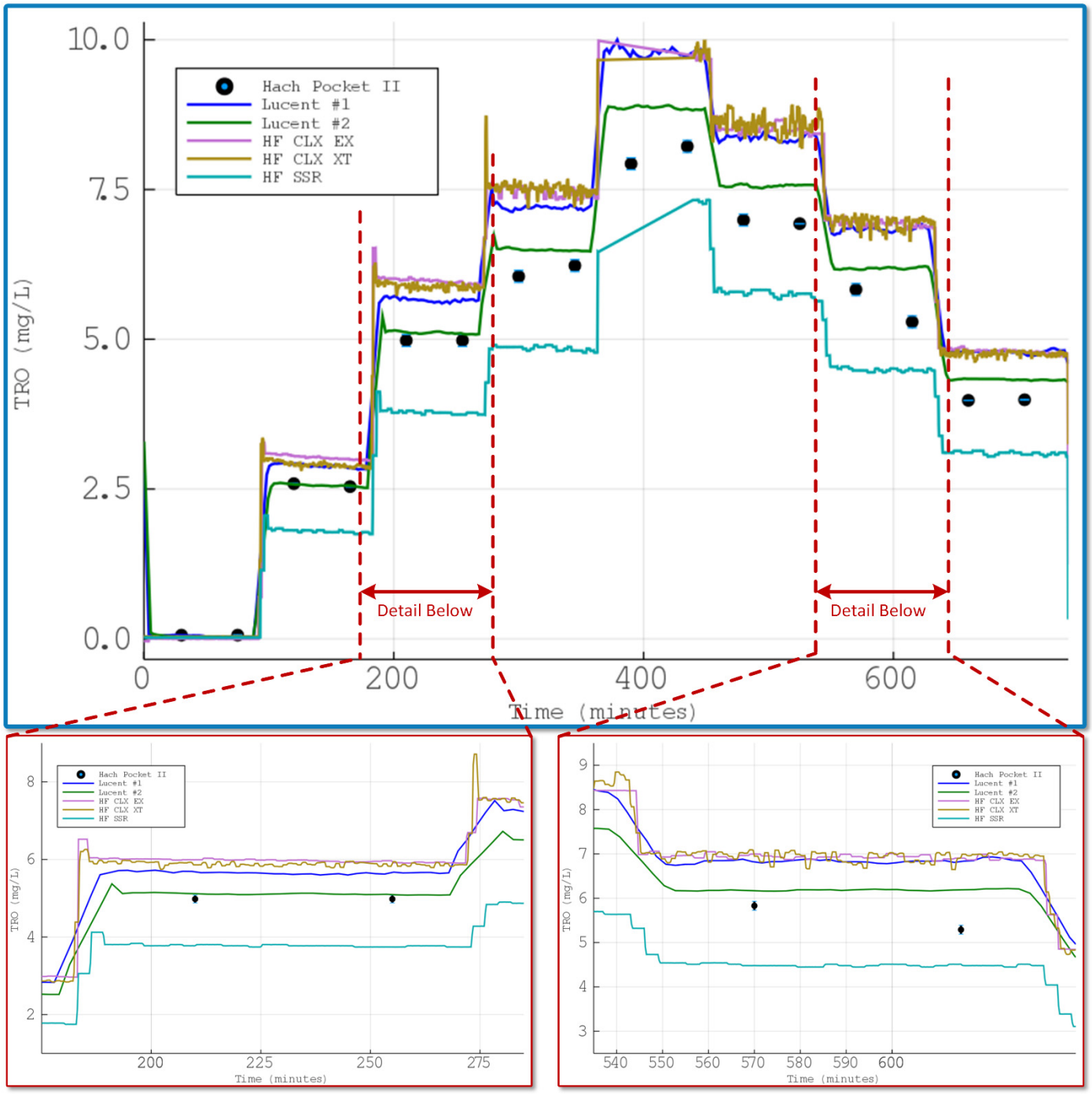


Figure 4: Data from brackish water, as recorded

Table 3: TRO Results – **Brackish water** (see **TRO RESULTS TABLE N** on page 13)

Original Data, Out-of-the-Box Operation

			Brackish Water				
Water Condition	**TOTAL Cl_2**	**FREE Cl_2**	**HF SSR**	**HF XT**	**HF EX**	**LW 1**	**LW 3**
Grab Sample 1, ppm	0.06	0.01	0.02	0.03	0.00	0.06	0.03
Grab Sample 2, ppm	0.06	0.01	0.02	0.03	0.00	0.03	0.03
Error (pppm)			-0.04	-0.03	-0.06	-0.02	-0.03
Grab Sample 3, ppm	2.59	2.24	1.81	2.89	3.05	2.91	2.59
Grab Sample 4, ppm	2.54	2.13	1.78	2.85	2.99	2.85	2.56
Error (pppm)	Free 85% of Total		-0.77	0.30	0.45	0.31	0.01
Grab Sample 5, ppm	4.98	4.26	3.80	5.86	5.99	5.70	5.12
Grab Sample 6, ppm	4.98	4.28	3.74	5.94	5.92	5.62	5.10
Error (pppm)	Free 86% of Total		-1.20	0.93	0.98	0.69	0.14
Grab Sample 7, ppm	6.05	5.56	4.87	7.60	7.51	7.19	6.51
Grab Sample 8, ppm	6.23	5.23	4.81	7.46	7.48	7.22	6.48
Error (pppm)	Free 88% of Total		-1.30	1.39	1.35	1.06	0.35
Grab Sample 9, ppm	7.93	7.12	>10	>10	>10	9.78	8.85
Grab Sample 10, ppm	8.22	7.29	>10	>10	>10	9.72	8.84
Error (pppm)	Free 89% of Total		---	---	---	1.68	0.77
Grab Sample 11, ppm	6.99	6.37	5.73	8.55	8.51	8.33	7.60
Grab Sample 12, ppm	6.93	6.14	5.76	8.23	8.66	8.32	7.57
Error (pppm)	Free 90% of Total		-1.22	1.43	1.63	1.36	0.62
Grab Sample 13, ppm	5.83	5.00	4.48	6.95	7.00	6.88	6.11
Grab Sample 14, ppm	5.29	4.79	4.48	6.99	6.91	6.81	6.19
Error (pppm)	Free 88% of Total		-1.08	1.41	1.39	1.29	0.59
Grab Sample 15, ppm	3.98	3.43	3.11	4.76	4.81	4.80	4.34
Grab Sample 16, ppm	3.99	3.33	3.08	4.79	4.80	4.77	4.32
Error (pppm)	Free 85% of Total		-0.89	0.79	0.82	0.80	0.35
Grab Sample 17, ppm							
Grab Sample 19, ppm							
Error (pppm)							
Per Experiment Error			**-0.93**	**0.89**	**0.94**	**0.90**	**0.35**
Per Experiment Sdev			**0.44**	**0.58**	**0.59**	**0.56**	**0.30**
Error - / + Sdev			-1.36 to -0.49	0.31 to 1.47	0.35 to 1.53	0.33 to 1.46	0.05 to 0.65

One-Point Span Corrected to Measurements at Brackish 6 ppm

			Brackish Water				
Water Condition	**TOTAL Cl_2**	**FREE Cl_2**	**HF SSR**	**HF XT**	**HF EX**	**LW 1**	**LW 3**
Grab Sample 1, ppm	0.06	0.01	0.03	0.03	0.00	0.05	0.03
Grab Sample 2, ppm	0.06	0.01	0.03	0.03	0.00	0.03	0.03
Error (pppm)			-0.03	-0.03	-0.06	-0.02	-0.03
Grab Sample 3, ppm	2.59	2.24	2.30	2.36	2.50	2.48	2.45
Grab Sample 4, ppm	2.54	2.13	2.26	2.33	2.45	2.43	2.42
Error (pppm)	Free 85% of Total		-0.29	-0.23	-0.09	-0.11	-0.13
Grab Sample 5, ppm	4.98	4.26	4.83	4.78	4.91	4.86	4.84
Grab Sample 6, ppm	4.98	4.28	4.75	4.84	4.85	4.79	4.82
Error (pppm)	Free 86% of Total		-0.19	-0.16	-0.09	-0.15	-0.14
Grab Sample 7, ppm	6.05	5.56	6.18	6.20	6.15	6.13	6.16
Grab Sample 8, ppm	6.23	5.23	6.10	6.08	6.13	6.15	6.13
Error (pppm)	Free 88% of Total		0.00	0.00	0.00	0.00	0.00
Grab Sample 9, ppm	7.93	7.12	>10	>10	>10	8.34	8.37
Grab Sample 10, ppm	8.22	7.29	>10	>10	>10	8.29	8.36
Error (pppm)	Free 89% of Total		---	---	---	0.24	0.29
Grab Sample 11, ppm	6.99	6.37	7.27	6.97	6.98	7.10	7.19
Grab Sample 12, ppm	6.93	6.14	7.30	6.71	7.10	7.09	7.16
Error (pppm)	Free 90% of Total		0.33	-0.12	0.08	0.14	0.21
Grab Sample 13, ppm	5.83	5.00	5.68	5.67	5.74	5.86	5.78
Grab Sample 14, ppm	5.29	4.79	5.68	5.70	5.66	5.80	5.85
Error (pppm)	Free 88% of Total		0.13	0.13	0.14	0.28	0.26
Grab Sample 15, ppm	3.98	3.43	3.94	3.88	3.94	4.09	4.10
Grab Sample 16, ppm	3.99	3.33	3.90	3.90	3.93	4.07	4.08
Error (pppm)	Free 85% of Total		-0.06	-0.09	-0.05	0.10	0.11
Grab Sample 17, ppm							
Grab Sample 19, ppm							
Error (pppm)							
Per Experiment Error			**-0.02**	**-0.07**	**-0.01**	**0.06**	**0.07**
Per Experiment Sdev			**0.20**	**0.12**	**0.09**	**0.16**	**0.17**
Error - / + Sdev			-0.22 to 0.18	-0.19 to 0.04	-0.10 to 0.08	-0.10 to 0.21	-0.10 to 0.24

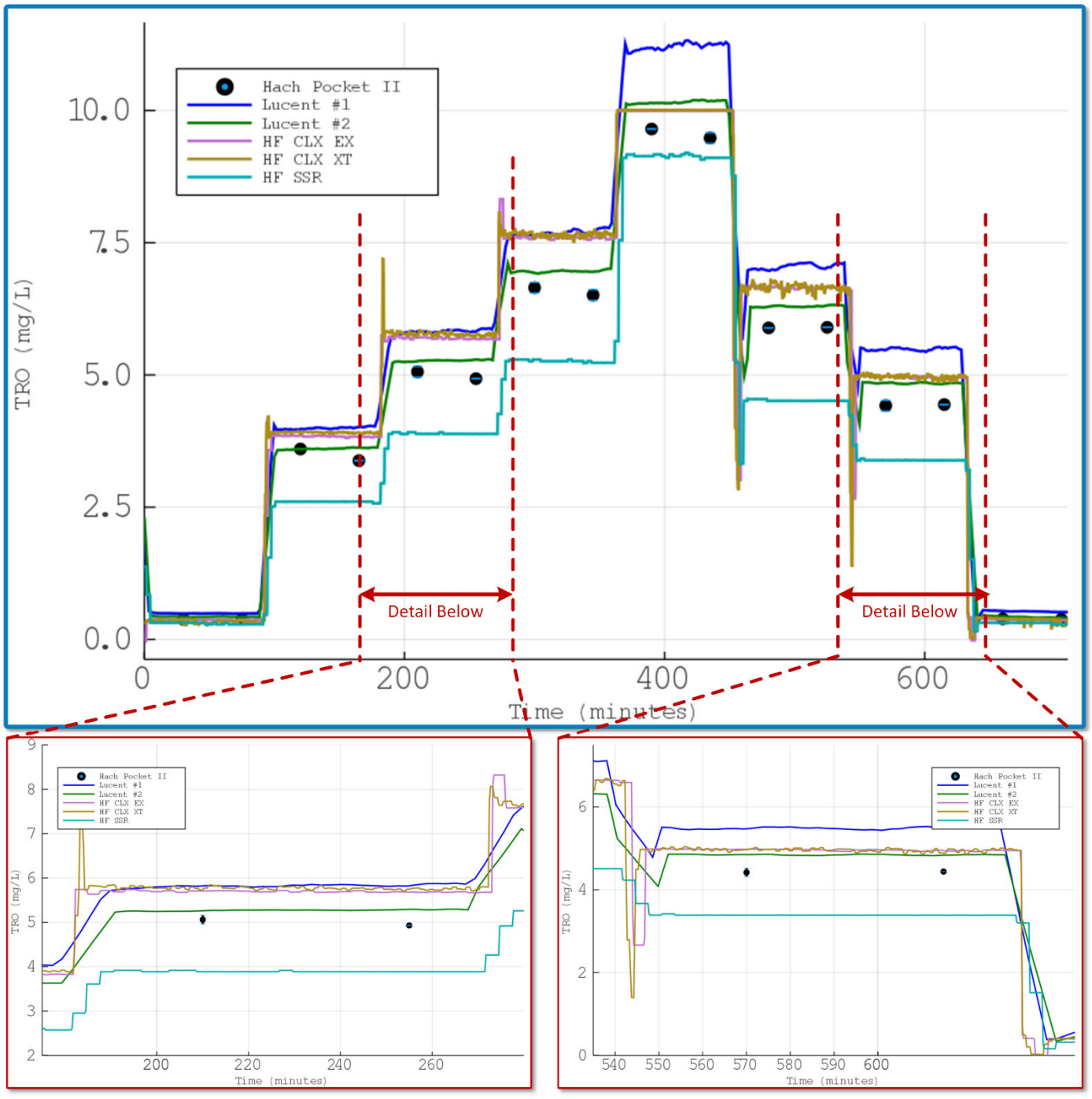


Figure 5: Data from fresh water, as recorded

Table 4: TRO Results – **Fresh water** (see **TRO RESULTS TABLE N** on page 13)

Original Data, Out-of-the-Box Operation

	Fresh Water						
Water Condition	**TOTAL Cl_2**	**FREE Cl_2**	**HF SSR**	**HF XT**	**HF EX**	**LW 1**	**LW 3**
Grab Sample 1, ppm	0.38	0.26	0.31	0.28	0.38	0.49	0.43
Grab Sample 2, ppm	0.38	0.26	0.28	0.35	0.37	0.49	0.42
Error (pppm)			-0.08	-0.07	-0.01	0.11	0.04
Grab Sample 3, ppm	3.60	3.16	2.60	3.88	3.85	3.97	3.60
Grab Sample 4, ppm	3.38	3.11	2.57	3.89	3.83	4.01	3.62
Error (pppm)	Free 90% of Total		-0.90	0.39	0.35	0.50	0.12
Grab Sample 5, ppm	5.06	4.56	3.89	5.77	5.71	5.82	5.25
Grab Sample 6, ppm	4.93	4.60	3.89	5.77	5.68	5.82	5.28
Error (pppm)	Free 92% of Total		-1.11	0.78	0.70	0.83	0.27
Grab Sample 7, ppm	6.65	6.24	5.29	7.61	7.59	7.62	6.94
Grab Sample 8, ppm	6.51	6.09	5.23	7.69	7.59	7.68	6.95
Error (pppm)	Free 94% of Total		-1.32	1.07	1.01	1.07	0.36
Grab Sample 9, ppm	9.65	8.79	9.14	10.01	9.99	11.18	10.13
Grab Sample 10, ppm	9.48	8.74	9.11	10.01	9.99	11.25	10.17
Error (pppm)	Free 92% of Total		-0.44	0.45	0.43	1.65	0.59
Grab Sample 11, ppm	5.89	5.39	4.51	6.60	6.68	6.98	6.28
Grab Sample 12, ppm	5.90	5.46	4.51	6.67	6.65	7.01	6.30
Error (pppm)	Free 92% of Total		-1.38	0.74	0.77	1.10	0.40
Grab Sample 13, ppm	4.42	4.03	3.39	4.97	4.98	5.48	4.85
Grab Sample 14, ppm	4.44	---	3.39	4.89	4.94	5.50	4.83
Error (pppm)	Free 91% of Total		-1.04	0.50	0.53	1.06	0.41
Grab Sample 15, ppm	0.39	---	0.32	0.39	0.38	0.54	0.44
Grab Sample 16, ppm	0.38	---	0.29	0.26	0.36	0.52	0.41
Error (pppm)			-0.08	-0.05	-0.01	0.15	0.04
Grab Sample 17, ppm							
Grab Sample 19, ppm							
Error (pppm)							
Per Experiment Error			**-0.80**	**0.48**	**0.47**	**0.81**	**0.28**
Per Experiment Sdev			**0.53**	**0.40**	**0.36**	**0.53**	**0.20**
Error - / + Sdev			-1.32 to -0.27	0.08 to 0.87	0.11 to 0.83	0.28 to 1.34	0.08 to 0.48

One-Point Span Corrected to Measurements at Brackish 6 ppm

	Fresh Water						
Water Condition	**TOTAL Cl_2**	**FREE Cl_2**	**HF SSR**	**HF XT**	**HF EX**	**LW 1**	**LW 3**
Grab Sample 1, ppm	0.38	0.26	0.40	0.23	0.31	0.42	0.41
Grab Sample 2, ppm	0.38	0.26	0.36	0.29	0.30	0.42	0.40
Error (pppm)			0.00	-0.12	-0.08	0.04	0.02
Grab Sample 3, ppm	3.60	3.16	3.30	3.16	3.16	3.38	3.40
Grab Sample 4, ppm	3.38	3.11	3.26	3.17	3.14	3.42	3.42
Error (pppm)	Free 90% of Total		-0.21	-0.32	-0.34	-0.09	-0.08
Grab Sample 5, ppm	5.06	4.56	4.93	4.71	4.68	4.96	4.96
Grab Sample 6, ppm	4.93	4.60	4.93	4.70	4.66	4.96	4.99
Error (pppm)	Free 92% of Total		-0.06	-0.29	-0.32	-0.03	-0.02
Grab Sample 7, ppm	6.65	6.24	6.71	6.20	6.23	6.50	6.56
Grab Sample 8, ppm	6.51	6.09	6.63	6.27	6.22	6.55	6.57
Error (pppm)	Free 94% of Total		0.09	-0.34	-0.36	-0.06	-0.01
Grab Sample 9, ppm	9.65	8.79	11.59	8.16	8.19	9.53	9.58
Grab Sample 10, ppm	9.48	8.74	11.55	8.16	8.19	9.59	9.62
Error (pppm)	Free 92% of Total		2.01	-1.40	-1.37	0.00	0.04
Grab Sample 11, ppm	5.89	5.39	5.72	5.38	5.47	5.95	5.94
Grab Sample 12, ppm	5.90	5.46	5.72	5.44	5.45	5.98	5.96
Error (pppm)	Free 92% of Total		-0.17	-0.49	-0.43	0.07	0.05
Grab Sample 13, ppm	4.42	4.03	4.30	4.06	4.08	4.67	4.59
Grab Sample 14, ppm	4.44	---	4.30	3.98	4.05	4.69	4.57
Error (pppm)	Free 91% of Total		-0.14	-0.41	-0.37	0.25	0.15
Grab Sample 15, ppm	0.39	---	0.40	0.32	0.31	0.46	0.42
Grab Sample 16, ppm	0.38	---	0.36	0.21	0.30	0.44	0.39
Error (pppm)			0.00	-0.11	-0.08	0.07	0.02
Grab Sample 17, ppm							
Grab Sample 19, ppm							
Error (pppm)							
Per Experiment Error			**0.19**	**-0.44**	**-0.42**	**0.03**	**0.02**
Per Experiment Sdev			**0.74**	**0.41**	**0.41**	**0.11**	**0.06**
Error - / + Sdev			-0.55 to 0.93	-0.85 to -0.03	-0.83 to -0.01	-0.08 to 0.14	-0.04 to 0.09

TRO RESULTS TABLE NOTES

1. The errors are presented as an absolute ppm value.

   Error is calculated with respect to the Grab Sample TOTAL value.

   When the TRO analyzer reading is less than the Grab Sample the error is a negative value.

   When the TRO analyzer reading is greater than the Grab Sample the error is a positive value.
2. On occasion the 4-20mA logger dropped signals; readings from the time of Grab Sample may be missing and disregarded from further calculation. Missing data is denoted by "---".
3. The HF Scientific XT and EX DPD analyzers cannot measure TRO greater than 10 ppm. Missing data is denoted by ">10".
4. The one-point span correction was performed using the data collected using the brackish data acquired at nominally 6 ppm. This data point was selected because it represented a value in middle of the acquired data (Day 6), using non-dechlorinated water, and at a TRO above 5 ppm.
5. The data for the one-point span calculation was performed as follows:

   Corrected Data Point = Original Data Point * Average TOTAL Grab Sample / Average Sensor Reading
6. All errors were evaluated and reported as an absolute error in ppm. This allows the data analysis to take into account all data acquired, including the zero readings. An analysis reporting error as a percentage of reading, or as a percentage of full-scale, can cause bias in the final interpretations. It is left to the discretion of the reader to perform any further interpretations. The Excel spreadsheet containing the calculations presented in the tables in this report is available upon request.

Table 5: Summary TRO Results

Original Data, Out-of-the-Box Operation

			Seawater				
Water Condition	TOTAL Cl_2	FREE Cl_2	HF SSR	HF XT	HF EX	LW 1	LW 3
Overall Average Error	0.19	all data	-0.95	0.65	0.73	0.44	0.08
Overall Average Sdev	0.13	all data	0.50	0.47	0.51	0.73	0.39
Error - / + Sdev	0.06 to 0.32	all data	-1.45 to -0.46	0.18 to 1.13	0.22 to 1.24	-0.29 to 1.17	-0.31 to 0.47

One-Point Span Corrected to Measurements at Brackish 6 ppm

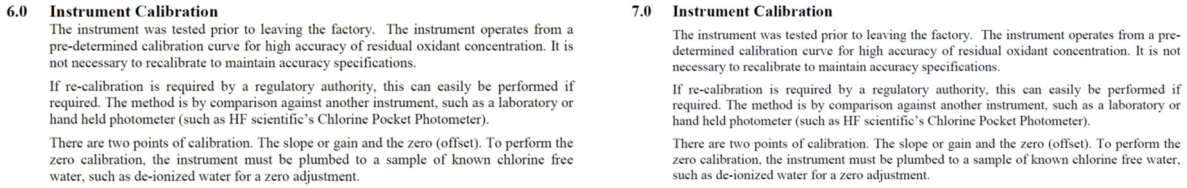
			Seawater				
Water Condition	TOTAL Cl_2	FREE Cl_2	HF SSR	HF XT	HF EX	LW 1	LW 3
Overall Average Error	-0.20	all data	0.01	-0.31	-0.22	-0.32	-0.18
Overall Average Sdev	0.13	all data	0.51	0.31	0.30	0.61	0.36
Error - / + Sdev	-0.34 to -0.07	all data	-0.49 to 0.52	-0.62 to 0.00	-0.52 to 0.08	-0.92 to 0.29	-0.54 to 0.18

CONCLUSIONS

OUT-OF-THE-BOX PERFORMANCE

The DPD analyzers had a significant deviation from the grab samples when operated with the default factory calibration. The errors observed were in excess of 1.00 ppm from the grab samples. This was unexpected. It had been expected that these analyzers could be operated with the reported accuracy out of the box.

Per the HF Scientific Manuals:



6.0 Instrument Calibration

The instrument was tested prior to leaving the factory. The instrument operates from a pre-determined calibration curve for high accuracy of residual oxidant concentration. It is not necessary to recalibrate to maintain accuracy specifications.

If re-calibration is required by a regulatory authority, this can easily be performed if required. The method is by comparison against another instrument, such as a laboratory or hand held photometer (such as HF scientific's Chlorine Pocket Photometer).

There are two points of calibration. The slope or gain and the zero (offset). To perform the zero calibration, the instrument must be plumbed to a sample of known chlorine free water, such as de-ionized water for a zero adjustment.

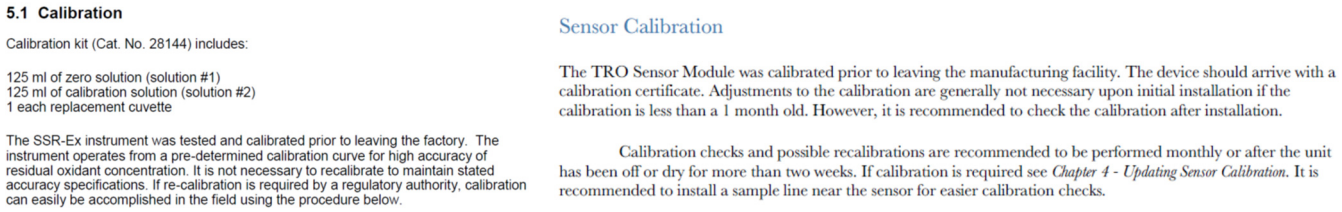
7.0 Instrument Calibration

The instrument was tested prior to leaving the factory. The instrument operates from a pre-determined calibration curve for high accuracy of residual oxidant concentration. It is not necessary to recalibrate to maintain accuracy specifications.

If re-calibration is required by a regulatory authority, this can easily be performed if required. The method is by comparison against another instrument, such as a laboratory or hand held photometer (such as HF scientific's Chlorine Pocket Photometer).

There are two points of calibration. The slope or gain and the zero (offset). To perform the zero calibration, the instrument must be plumbed to a sample of known chlorine free water, such as de-ionized water for a zero adjustment.

Figure 6: Instrument Calibration section of the HF Scientific CLX-XT (left) and CLX-EX (right) manuals.



5.1 Calibration

Calibration kit (Cat. No. 28144) includes:

125 ml of zero solution (solution #1)
125 ml of calibration solution (solution #2)
1 each replacement cuvette

The SSR-Ex instrument was tested and calibrated prior to leaving the factory. The instrument operates from a pre-determined calibration curve for high accuracy of residual oxidant concentration. It is not necessary to recalibrate to maintain stated accuracy specifications. If re-calibration is required by a regulatory authority, calibration can easily be accomplished in the field using the procedure below.

Sensor Calibration

The TRO Sensor Module was calibrated prior to leaving the manufacturing facility. The device should arrive with a calibration certificate. Adjustments to the calibration are generally not necessary upon initial installation if the calibration is less than a 1 month old. However, it is recommended to check the calibration after installation.

Calibration checks and possible recalibrations are recommended to be performed monthly or after the unit has been off or dry for more than two weeks. If calibration is required see *Chapter 4 - Updating Sensor Calibration*. It is recommended to install a sample line near the sensor for easier calibration checks.

Figure 7: Calibration section of the HF Scientific SSR manual (left) and the Lucent Water manual (right).

The amperometric analyzers performed slightly better out-of-the-box in a fashion that is supported by the calibration statement in the manual; the sensors were less than one month old.

The performance of the HF Scientific and Lucent Water TRO analyzers when deployed out-of-the-box were similar with regard to their error with respect to the grab samples. The data graphs, however, illustrate the signal to noise improvement gained by using data averaging – this was enabled on the amperometric analyzers and not on the DPD analyzers. All of the evaluated analyzers can perform signal averaging and it is advisable to enable this signal averaging unless it is critical to observe sudden temporal TRO changes.

SPAN CORRECTED PERFORMANCE

After performing the span correction, the observed analyzer errors, while significantly reduced compared to the out-of-box errors, generally exceed the measurement accuracy reported by the respective manufacturers. This statement is made with regard to assessing the overall error over the duration of the entire data set across all three water salinities.

However, the overall error reported by the amperometric analyzers appear to be indistinguishably different from the errors reported by the DPD analyzers. Additionally, the new SSR DPD analyzer error appears to be comparable to the older DPD analyzers. From the analysis these analyzers demonstrated comparable performance.

GENERAL COMMENTS

Despite differences in the sample rates, measurement technique, and sample flow rates, over the entire evaluation period the TRO analyzers units reported a similar range of errors. While there are significant differences in the installation requirements for the various analyzers, it appears that the selection of analyzers offers more application choices as compared to when we performed a similar TRO Analyzer evaluation in the Fall of 2018.

END OF TEST REPORT