# THE ENVIRONMENTAL TECHNOLOGY VERIFICATION







## **ETV Joint Verification Statement**

TECHNOLOGY TYPE: MULTI-PARAMETER WATER QUALITY PROBE

APPLICATION: MEASURING WATER QUALITY

**TECHNOLOGY NAME: Ocean Seven 316** 

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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative or improved environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations; with stakeholder groups, consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The Advanced Monitoring Systems (AMS) Center, one of seven technology areas under ETV, is operated by Battelle in cooperation with EPA's National Exposure Research Laboratory. The AMS Center has recently evaluated the performance of multi-parameter water probes. This verification statement provides a summary of the test results for the General Oceanics, Inc., Ocean Seven 316 water probe.

### VERIFICATION TEST DESCRIPTION

The Ocean Seven 316 was evaluated by comparing pre- and post-calibration results and their measurements with standard reference measurements and handheld calibrated probes. The Ocean Seven 316 was deployed in saltwater, freshwater, and laboratory environments near Charleston, South Carolina, during a 2 ½-month verification test. Water quality parameters were measured both by two Ocean Seven 316s and by reference measurements consisting of field-portable instrumentation and water analyses of collected water samples. During each phase, performance was assessed in terms of pre- and post-calibration results, relative bias, precision, linearity, and inter-unit reproducibility. The saltwater site was at the National Oceanic and Atmospheric Adminstration (NOAA) Pier Romeo on the Cooper River, the freshwater site was at Lake Edmunds, approximately one mile from the NOAA Center for Coastal Environmental Health and Biomolecular Research (CCEHBR), and the controlled site was the CCEHBR mesocosm facility in Charleston, South Carolina. Test parameters included dissolved oxygen (DO), conductivity, temperature, pH, and turbidity.

Saltwater testing was conducted at two locations. The original location was in a small tidal creek tributary of the Charleston Harbor. However, due to structural problems at that site, the probes were redeployed at the NOAA Pier Romeo on the Cooper River. Pre- and post-calibration data obtained at the first location are presented in the verification report; however, no reference data from that location are presented. The saltwater test lasted for 31 days, during which time the Ocean Seven 316s monitored the naturally occurring range of the target parameters, collecting data every 15 minutes, 24 hours a day, except on days when the probes were in the laboratory for preand post-calibration checks. Reference sample collection times were rotated among the morning, afternoon, and evening hours throughout the test. More intense sampling occurred at the beginning (Days 1 and 2) and the end (Days 29 and 30) of the sampling period when samples were taken at 15-minute intervals for eight hours, except on Day 29, when only four hours of sampling occurred because of weather conditions. For the duration of the saltwater test, the Ocean Seven 316s were deployed at depths between approximately three and 10 feet, varying according to the tide. Freshwater testing was conducted at Lake Edmunds. Because this site is shallower than the Cooper River, only one depth (approximately 3 feet) was used; however, the same sample collection schedule was followed. As in the saltwater portion of the verification test, the Ocean Seven 316s monitored the naturally occurring target parameters, while simultaneous reference measurements were made, again rotating among collection times. More intense sampling occurred at the beginning (Day 3) and the end (Day 23) of the sampling period, when samples were taken at 15- to 30-minute intervals for periods ranging between six and eight hours, as weather permitted. The third, and final, stage of testing occurred at the CCEHBR mesocosm facility. The mesocosm tanks were filled with saltwater/freshwater and drained daily, simulating a tide. Water samples were collected during each test day throughout the normal operating hours of the facility (nominally 6 a.m. to 6 p.m.). During this period, the mesocosm was manipulated to introduce variations in the measured parameters. The turbidity of the system was varied by operating a pump near the sediment trays to suspend additional solids in the water. Conductivity was varied by adding freshwater to the saltwater during one of the fill-and-drain cycles. Variations in temperature, pH, and DO were driven by natural forces and the changes in the other test parameters. Over all three sampling periods, approximately 6,000 data points were collected by the Ocean Seven 316s, and 132 sets of reference measurements were obtained.

QA oversight of verification testing was provided by Battelle. Battelle QA staff conducted a technical systems audit, a performance evaluation audit, and a data quality audit of 10% of the test data.

#### TECHNOLOGY DESCRIPTION

The following description of the Ocean Seven 316 was provided by the vendor and does not represent verified information. The 16-bit, multi-parameter Ocean Seven 316 is available with two diameters: 100 millimeters (mm) and 75 mm. The measurement sensors have time constants of 50 milliseconds (ms) for physical parameters and 3 seconds (s) for chemical parameters. A high-precision resistor acts as a reference for the accuracy of the sensor electronic amplifiers. This resistor has a thermal drift of 1 part per million/°C and is temperature-compensated. The Ocean Seven 316 is microprocessor-controlled and can measure, store, and transmit sensor data. For real-time data acquisition, the Ocean Seven 316 operates unattended, and data are uploaded at the end of the measuring cycle. An automatic power management procedure switches the Ocean Seven 316 off between the data acquisitions. The internal battery package consists of 10 batteries that allow the Ocean Seven 316 to operate continuously for about 20 hours. The Ocean Seven 316 can be equipped with an external battery package that greatly extends operation time. The Ocean Seven 316 stores up to 32,000 data sets and is equipped with sensors to measure pressure, temperature, conductivity, salinity, oxygen, pH, and oxidation-reduction potential. Salinity is automatically calculated from conductivity, temperature, and pressure values.

#### VERIFICATION OF PERFORMANCE

**Pre-and post-calibration results:** Pre-and post-calibration tests were performed for pH, DO, and conductivity since only those parameters are adjusted during calibration. The results showed that pH measurement values were accurate within a range of 99 to 108% of the true values, DO measurement values were accurate within a range of 82 to 105% of the true values, and conductivity measurement values were accurate within a range of 94 to 104% of the true values.

**Relative bias:** A summary of the average relative bias for each deployment setting is provided in the table below. The temperature biases were less than or equal to 0.11% for all deployment settings. Conductivity, pH (reported as H<sup>+</sup> concentration), and DO biases were between 2 and 36% for both units under all deployment settings. The conductivity bias was consistently positive, indicating that generally, the Ocean Seven 316s reported a higher conductivity than the handheld reference probe. The DO bias was consistently negative for each deployment setting. The bias for turbidity ranged between -44% and 420%.

		Salt	water	Fresh	ıwater	Mesocosm		
Parameter	Units	% Rel. Bias GO Probe #1	% Rel. Bias GO Probe #2	% Rel. Bias GO Probe #1	% Rel. Bias GO Probe #2	% Rel. Bias GO Probe #1	% Rel. Bias GO Probe #2	
Temperature	K	-0.09	-0.06	-0.11	-0.03	-0.07	-0.09	
Conductivity	mS/cm	21.5	10.6	9.21	15.1	2.62	1.96	
DO	mg/L	-21.9	-24.8	-28.6	-20.4	-6.19	-15.3	
H+	mol/L	28.2	28.8	35.5	-23.9	-20.3	-31.2	
Turbidity	NTU	269	-43.9	318	420	146	111	

**Precision:** Precision was determined during the mesocosm deployments and is reported as percent relative standard deviation (%RSD). The %RSD values were lowest for pH and temperature, ranging between 0.02%RSD and 0.07%RSD. Precision for conductivity was 1.08%RSD and 1.07%RSD for the two Ocean Seven 316s. Precision values were not determined for DO or turbidity because data from stable periods of operation were not available for analysis.

**Linearity:** Linearity was assessed by comparing probe readings against the reference values for each of the parameters at each deployment location. The table below provides the results of this comparison by showing the slope, intercept, and coefficient of determination  $(r^2)$  at each site for the Ocean Seven 316. Linearity was highest for conductivity and temperature, with a strong correlation for most of the parameters during mesocosm deployment, with most  $r^2$  values greater than 0.84.

GO Saltwater		Freshwater			Mesocosm					
Probe #	Parameter	Slope	Intercept	r <sup>2</sup>	Slope	Intercept	$\mathbf{r}^2$	Slope	Intercept	$\mathbf{r}^2$
1	Temp	0.93	20.49	0.85	0.96	10.92	0.99	0.97	9.35	0.98
2	Temp	0.94	18.47	0.86	0.91	28.11	0.91	0.85	45.84	0.95
1	Cond	1.17	-1.59	0.92	1.23	-0.05	0.93	1.05	-0.08	0.99
2	Cond	1.17	-1.55	0.92	1.19	-0.01	0.93	1.04	-0.09	1.00
1	DO	0.16	3.15	0.06	0.67	0.33	0.66	0.97	-0.22	0.56
2	DO	0.36	1.95	0.12	0.82	-0.10	0.92	0.63	1.39	0.66
1	pН	0.94	0.00	0.55	0.26	0.00	0.53	0.62	0.00	0.88
2	pН	0.94	0.00	0.55	0.48	0.00	0.78	0.62	0.00	0.84
1	Turb	0.63	7.67	0.05	2.64	10.18	0.14	1.05	5.88	0.88
2	Turb	0.49	0.43	0.12	4.86	0.21	0.32	1.09	5.42	0.85

**Inter-unit reproducibility:** Analysis of inter-unit reproducibility, presented in the table below, showed that the average difference in temperature readings between the two Ocean Seven 316s tested was 0.08°C, over a range of 24 to 34°C. The difference in conductivity averaged 0.04 mS/cm over a range of 0.3 to 44 mS/cm. Analysis of inter-unit reproducibility showed that the average difference in readings for DO was 0.55 mg/L, while the Ocean Seven 316 DO readings varied from 3 to 15 mg/L. The average difference in pH readings was 0.12 over a range of 6.8 to 8.7. The average difference in turbidity readings was 8.96 NTU, while the actual turbidity measurement ranged from 0 to 197 NTU. The magnitude of the inter-unit reproducibility results was affected by spatial and temporal changes in the sampling environment. For example, the Ocean Seven 316s were sampling in an environment that was changing 8°C over a 24-hour period. Because the Ocean Seven 316s were not sampling in exactly the same location, differences in temperature, caused by the 24-hour fluctuations, resulted in some difference in measurement by the Ocean Seven 316s. Similar behavior occurs in any location that experiences dynamic changes in the environment. The comparison of relative bias (as described above) is also a measure of inter-unit reproducibility. The relative biases of the two Ocean Seven 316s were comparable for temperature, DO, and conductivity, but showed larger differences for pH (freshwater only) and turbidity.

	Average Difference between GO Probe #1 and GO Probe #2					
Location	Temperature °C	Conductivity (mS/cm)	DO (mg/L)	pН	Turbidity (NTU)	
Saltwater	0.01	0.10	0.34	0.07	8.18	
Freshwater	0.11	0.02	0.60	0.24	17.67	
Mesocosm	0.13	0.01	0.71	0.06	1.02	
Average	0.08	0.04	0.55	0.12	8.96	

<b>Other factors:</b> The probes were set up to collect data with minimal difficulty, and data were downloaded without incident using the provided data cable and a Windows-based PC. The Ocean Seven 316s verified in this test cost \$15,000 per unit.						
original signed by Gabor J. Kovacs	3/21/03	original signed by Gary J. Foley	4/29/03			
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