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Tech Note

YSI pH Sensor Performance

The accurate, reliable measurement of pH in environmental water is important to the majority of users of YSI 6-Series multiparameter instruments. YSI instruments are used to sample or continuously monitor water with a wide range of conductivities. These range from seawater with a conductivity of 53,000 µS/cm, to "average" freshwater lakes and rivers with conductivities of 200 to 1500 µS/cm, to pure mountain streams with conductivities as low as 15 µS/cm. YSI pH sensors have been carefully designed to perform under all of these ionic strength conditions, including low conductivity water which has historically been the most difficult medium with respect to accuracy, quick response to pH changes, and minimal flow dependence.

YSI offers the 6561 (pH only) and 6565 (pH/ORP) for use with the 600XL, 600XLM, 6820, 6920, 6600, 6600EDS, and ADV6600; the 6580/6581 system for the 600R and 600QS, and the 6031 for the 6000. The goal of this technical note is to provide documentation related to the performance of these pH sensors. The three studies outlined below were designed to test the accuracy, response time, and flow dependence of these sensors in media of varying conductivities with the emphasis on these parameters in low ionic strength water. The results presented are typical of more extensive evaluations of these sensors and indicate that YSI pH systems will provide excellent field performance for our users in waters of varying conductivities without the need for probes which are specially-designed (and expensive) for low ionic strength applications.

This application provides performance documentation of the two new pH sensors available for the 6-Series Product line and the 6031 sensor for the 6000. The three studies outlined below were designed to test the accuracy, response time, and flow dependence of these sensors in media of varying conductivities. The emphasis is on water with low conductivity. YSI feels that the results presented (which correlate with more extensive evaluations) indicate that the 6561, 6565, and 6580/6581 pH systems will provide excellent field performance in waters of varying conductivities and eliminate the need for expensive probes that are specially designed for low conductivity applications.

Study 1

Rainwater samples (2694-I and 2694-II) of certified pH were purchased from the NIST. A conductivity of 25.4 µS/cm and a true pH of 4.3 characterized sample 2694-I; sample 2694-II had a conductivity of 129 µS/cm and a true pH of 3.6. After calibration of the 6561 and 6031 sensors with pH 4 and pH 7 standard buffers, the probes were placed in the unstirred NIST rainwater samples and the observed pH monitored with time. The water was then stirred while continuing to monitor the pH readings. The results of the study are found in Tables 1 and 2 below.

Time, min	Stirring	6031 Obs. pH
0.5	Off	4.23
1	Off	4.25
2	Off	4.26
3	Off	4.22
4	Off	4.22
5	Off	4.22
5.5	On	4.20
6	On	4.21
7	On	4.22
8	On	4.22

Time, min	Stirring	6561 Obs. pH
0.5	Off	4.7
1	Off	4.43
2	Off	4.30
4	Off	4.26
8	Off	4.23
9	On	4.19
10	On	4.18
11	On	4.17
12	On	4.16
13	On	4.16

Table 1. YSI pH sensor evaluation in NIST standard 2694-I. (Sp. Cond. = 25.4 µS/cm; pH = 4.3)

Time, min	Stirring	6031 Obs. pH
0.5	Off	3.54
1	Off	3.55
2	Off	3.55
2.5	On	3.54
3	On	3.54
4	On	3.54

Time, min	Stirring	6561 Obs. pH
0.5	Off	3.60
1	Off	3.58
2	Off	3.56
3	Off	3.55
4	Off	3.54
5	Off	3.54
6	Off	3.52
6.5	On	3.52
7	On	3.51
8	On	3.51

Table 2. YSI pH sensor evaluation in NIST standard 2694-II. (Sp. Cond. = 129 µS/cm; pH = 3.6)

Note: In both rainwater standards: (1) the pH readings stabilized quickly after transfer from the high conductivity pH 7 buffer to the low conductivity water; (2) the pH readings exhibited minimal stirring dependence; and (3) the final pH values for both sensors were within 0.15 pH units of the true values after stabilization.

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Study 2

In this study, environmental water samples of low conductivity were obtained from one of our customers for evaluation of the response time and flow dependence of the 6561 and 6031 pH sensors. The first and second samples had specific conductance values of 15 and 60 µS/cm, respectively. As in the first study, the sensors were calibrated in pH 4 and pH 7 standard buffers and then the probes were placed in the test samples. The stabilization pattern was monitored under stirred conditions, and the stirring was deactivated and then reactivated over a total time period of 17 minutes. Results are displayed in Tables 3 and 4 below.

Time, min	Stirring	6561 Obs. pH	6031 Obs. pH
0	On	5.90	5.88
0.5	On	6.33	6.35
1	On	6.50	6.51
2	On	6.65	6.63
5	On	6.76	6.74
5.5	On	6.81	6.83
6	Off	6.81	6.84
7	Off	6.82	6.79
10	Off	6.82	6.64
15	On	6.82	6.75
17	On	6.79	6.80

Table 3. YSI pH sensor evaluation in environmental sample #1. (Sp. Cond. = 15 µS/cm)

Time, min	Stirring	6561 Obs. pH	6031 Obs. pH
0	On	7.58	7.03
0.5	On	7.39	7.03
1	On	7.29	7.02
2	On	7.22	7.05
5	On	7.21	7.09
5.5	Off	7.24	7.15
6	Off	7.24	7.16
7	Off	7.24	7.16
10	Off	7.23	7.15
12	On	7.23	7.11

Table 4. YSI pH sensor evaluation in environmental sample #2. (Sp. Cond. = 63 µS/cm)

Note: (1) the pH readings stabilized quickly on transfer from the high conductivity buffer to the low conductivity water sample; (2) the pH readings exhibited minimal flow dependence; and (3) the final pH of the two sensors agreed within approximately 0.1 pH unit in both low conductivity water samples. The true pH of the sample was not certified, but the customer considered the final pH values reasonable based on past experience.

Study 3

In this study, samples of varying conductivities were prepared by diluting local tap water with deionized water (to simulate low ionic strength samples) or by adding sodium chloride to local tap water (to simulate seawater). Prior to the experiments, the mixtures were saturated with air to assure a final stable pH for the water samples. The sensors to be evaluated were calibrated in pH 7 and pH 10 standard buffers and then placed in the test samples. As above, the stabilization pattern was monitored under stirred conditions, and the stirring was deactivated and then reactivated over a total time period of 12 minutes. In these experiments, two 6561 sensors and one 6031 sensor were evaluated for response time and flow dependence. Results are displayed in Tables 5-8 below.

Time, min	Stirring	6561-1 Obs. pH	6561-2 Obs. pH	6031 Obs. pH
0	On	7.28	7.38	7.65
0.5	On	7.28	7.37	7.43
1	On	7.29	7.34	7.36
2	On	7.28	7.31	7.32
5	On	7.29	7.30	7.29
5.5	Off	7.31	7.33	7.34
6	Off	7.31	7.33	7.34
7	Off	7.30	7.33	7.31
10	Off	7.30	7.31	7.33
12	On	7.29	7.31	7.28

Table 5. YSI pH sensor evaluation in laboratory sample #1. (Sp. Cond. = 45 µS/cm)

Note that: (1) the pH readings stabilized quickly on transfer from the high conductivity buffer to water samples regardless of conductivity; (2) the pH readings exhibited minimal flow dependence in all media; and (3) the final pH values of the three sensors agreed within 0.1 pH unit in each of water samples which span a wide conductivity range. As in the second study above, the true pH of the samples was not certified, but the readings appeared reasonable based on our past experience, and the excellent agreement between sensors provides indirect evidence that the sensors are likely to be accurate.

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Time, min	Stirring	6561-1 Obs. pH	6561-2 Obs. pH	6031 Obs. pH
0	On	7.91	7.90	7.89
0.5	On	7.96	8.03	7.93
1	On	8.02	8.06	7.97
2	On	8.08	8.10	8.02
5	On	.14	8.13	8.05
5.5	Off	8.15	8.15	8.16
6	Off	8.15	8.15	8.16
7	Off	8.16	8.15	8.16
10	Off	8.15	8.15	8.17
12	On	8.16	8.15	8.06

Table 6. YSI pH sensor evaluation in laboratory sample #2. (Sp. Cond. = 260 µS/cm)

Time, min	Stirring	6561-1 Obs. pH	6561-2 Obs. pH	6031 Obs. pH
0	On	8.41	8.44	8.35
0.5	On	8.50	8.51	8.42
1	On	8.54	8.55	8.46
2	On	8.56	8.57	8.50
5	On	8.58	8.60	8.54
5.5	Off	8.59	8.61	8.59
6	Off	8.59	8.61	8.59
7	Off	8.60	8.61	8.59
10	Off	8.60	8.62	8.60
12	On	8.60	8.62	8.54

Table 7. YSI pH sensor evaluation in laboratory sample #3. (Sp. Cond. = 860 µS/cm)

Time, min	Stirring	6561-1 Obs. pH	6561-2 Obs. pH	6031 Obs. pH
0	On	8.22	8.22	8.20
0.5	On	8.24	8.25	8.29
1	On	8.25	8.27	8.30
2	On	8.27	8.28	8.30
5	On	8.29	8.29	8.31
5.5	Off	8.29	8.29	8.32
6	Off	8.30	8.29	8.32
7	Off	8.30	8.29	8.32
10	Off	8.30	8.30	8.32
12	On	8.30	8.30	8.32

Table 8. YSI pH sensor evaluation in laboratory sample #4. (Sp. Cond. = 53,000 µS/cm)

Summary

YSI feels that the above experiments provide evidence that our standard pH sensors will yield reliable and accurate readings in field samples over a wide conductivity range with no additional requirement for custom (and higher cost) sensors for special ionic strength conditions. The first study shows that the 6561 and 6031 sensors agree well in terms of absolute accuracy with certified low conductivity NIST rainwater standards, perhaps the most difficult field application, as well a providing fast response and minimal flow dependence.

The second study confirms the fast response and low flow dependence of the sensors in actual environmental samples of low conductivity. The third study shows that these key desirable characteristics are observed in prepared water samples over a wide conductivity range of 45 µS/cm to 53,000 µS/cm (low ionic strength freshwater to seawater). While not tested in the above studies, it is likely that the performance of the 6565 combination pH/ORP sensor and the Model 600 pH system (which is characterized by a replaceable reference electrode module) will be similar to those described for the 6561, since the reference junction of the two systems is identical with that of the 6561.

Although YSI cannot guarantee that all sensors will perform as well as those described in every environmental application, YSI feels that these results are typical. Remember, however, that the long-term performance of any pH sensor will be dependent on the environmental conditions under which the sensor is used. For example, sensor performance may deteriorate somewhat more rapidly with time if heavy biological fouling occurs in monitoring studies, necessitating more frequent probe replacement to obtain the level of accuracy and response time shown above. In addition, be sure to follow YSI recommendations for pH probe storage to maintain good performance and maximize the lifetime of your sensor.

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