Technical Note

pH Calibration Procedure for Optimal Measurement Precision

Key Words

- pH
- Calibration
- Precision

Introduction

This technical note provides a general calibration procedure for the best pH measurement precision.

Recommended Equipment

1. pH meter
2. pH electrode
3. NIST traceable thermometer or ATC probe
4. Magnetic stir plate and stir bar or Thermo Scientific Orion stirrer probe
5. 50 mL beakers and 200 mL waste beakers
6. Watch glasses or parafilm
7. pH 4.01 buffer
8. pH 7.00 buffer
9. pH 10.01 buffer
10. Deionized water

Calibration Buffer Preparation

1. Pour about 30 mL of pH 10.01 buffer into a 50 mL beaker and cover the beaker with a watch glass or parafilm prior to calibration.
2. Pour about 30 mL of pH 7.00 buffer into a 50 mL beaker and cover the beaker with a watch glass or parafilm prior to calibration.
3. Pour about 30 mL of pH 4.01 buffer into a 50 mL beaker and cover the beaker with a watch glass or parafilm prior to calibration.
4. Pour about 30 mL each of the pH 10.01, 7.00 and 4.01 buffers into separate 50 mL beakers. Use these three beakers as the rinse beakers during calibration.
5. Allow all of the buffers to reach the same temperature, since pH readings are temperature dependant.

Sample Preparation

1. Collect and prepare the samples according your sample requirements and procedures.
2. Pour about 30 mL of the sample into a 50 mL beaker, label the beaker and cover the beaker with a watch glass or parafilm prior to sample measurements. Repeat this step for all of the samples.
3. Pour about 30 mL of each sample into separate 50 mL beakers and label the beakers. Use these sample beakers as the rinse beakers during sample measurements.
4. Allow all of the samples to reach the same temperature, since pH readings are temperature dependant.

Electrode Preparation

Prepare the electrode according to the instructions in the electrode user guide or instruction manual. Prior to calibration, store the electrode in pH electrode storage solution, Cat. No. 910001; ROSS pH electrode storage solution, Cat. No. 810001; or 100 mL of pH 7 buffer with 0.5 g of potassium chloride (KCl) added.

Meter Setup

Prepare the meter according to the instructions in the meter user guide or instruction manual. Make sure that the correct meter settings are selected for your sample requirements and procedures.

Calibration

1. Allow all of the buffers to reach the same temperature, since pH readings are temperature dependant. If the buffers are not at 25 °C, temperature compensation is recommended. Measure the temperature of the buffers using a NIST traceable thermometer and manually enter the temperature into the meter or use an ATC probe to automatically transmit the temperature of the buffers to the meter.
2. Prepare the pH 10.01 buffer, pH 7.00 buffer and pH 4.01 buffer as described in the Calibration Buffer Preparation section and uncover the calibration beakers.
3. Rinse the pH electrode first with deionized water and then in the pH 10.01 buffer rinse beaker. Make sure to rinse the electrode with deionized water over a waste beaker to prevent contamination of the buffers. The electrode should never be rinsed in the same buffer beaker that will be used for calibration.
4. Place the electrode into the pH 10.01 buffer calibration beaker, so the electrode tip and junction are fully immersed in the buffer, and stir the buffer at a moderate, uniform rate.
5. Start the calibration on the meter.
6. Wait for a stable reading in the pH 10.01 buffer, at least 1 to 2 minutes. If the temperature of the buffer was entered manually or an ATC probe is in use, the meter should automatically recognize the buffer and display its temperature-corrected pH value. If the meter does not automatically recognize the buffer, enter the value of the pH buffer at its measured temperature using **Table 1** on the right.
7. Once the correct buffer value is entered, prompt the meter to proceed to the next calibration point.
8. Rinse the pH electrode first with deionized water and then in the pH 7.00 buffer rinse beaker. Make sure to rinse the electrode with deionized water over a waste beaker to prevent contamination of the buffers. The electrode should never be rinsed in the same buffer beaker that will be used for calibration.
9. Place the electrode into the pH 7.00 buffer calibration beaker, so the electrode tip and junction are fully immersed in the buffer, and stir the buffer at a moderate, uniform rate.
10. Wait for a stable reading in the pH 7.00 buffer, at least 1 to 2 minutes. If the temperature of the buffer was entered manually or an ATC probe is in use, the meter should automatically recognize the buffer and display its temperature-corrected pH value. If the meter does not automatically recognize the buffer, enter the value of the pH buffer at its measured temperature using **Table 1** on the right.
11. Once the correct buffer value is entered, prompt the meter to proceed to the next calibration point.
12. Rinse the pH electrode first with deionized water and then in the pH 4.01 buffer rinse beaker. Make sure to rinse the electrode with deionized water over a waste beaker to prevent contamination of the buffers. The electrode should never be rinsed in the same buffer beaker that will be used for calibration.
13. Place the electrode into the pH 4.01 buffer calibration beaker, so the electrode tip and junction are fully immersed in the buffer, and stir the buffer at a moderate, uniform rate.
14. Wait for a stable reading in the pH 4.01 buffer, at least 1 to 2 minutes. If the temperature of the buffer was entered manually or an ATC probe is in use, the meter should automatically recognize the buffer and display its temperature-corrected pH value. If the meter does not automatically recognize the buffer, enter the value of the pH buffer at its measured temperature using **Table 1** on the right.
15. Once the correct buffer value is entered, prompt the meter to save and end the calibration.
16. Rinse the pH electrode with deionized water and store the electrode in pH electrode storage solution. Cover the calibration beakers with a watch glass or parafilm.

Calibration Verification

1. Use the same buffers that were used for calibration or prepare fresh buffers as described in the Calibration Buffer Preparation section. Uncover the calibration verification beakers.
2. Rinse the pH electrode first with deionized water and then in the pH 10.01 buffer rinse beaker. Make sure to rinse the electrode with deionized water over a waste beaker to prevent contamination of the buffers. The electrode should never be rinsed in the same buffer beaker that will be used for calibration verification.
3. Place the electrode into the pH 10.01 buffer calibration verification beaker, so the electrode tip and junction are fully immersed in the buffer, and stir the buffer at a moderate, uniform rate.
4. Start the measurement on the meter.
5. Wait for a stable reading, at least 1 to 2 minutes, and then record the pH and temperature of the buffer.
6. Repeat steps 2 through 5 for the pH 7.00 buffer and then the pH 4.01 buffer.
7. Compare the recorded pH and temperature values of the buffers to those listed in **Table 1** on the right.
8. Rinse the pH electrode with deionized water and store the electrode in pH electrode storage solution until the samples are ready for measurement.

Table 1 – pH Buffer Values at Various Temperatures

Temp. (°C)	pH 10.01 Buffer	pH 7.00 Buffer	pH 4.01 Buffer
0	10.320	7.111	4.000
1	10.305	7.105	4.000
2	10.291	7.099	3.999
3	10.277	7.093	3.999
4	10.262	7.088	3.999
5	10.249	7.082	3.999
6	10.235	7.077	3.999
7	10.221	7.071	3.999
8	10.208	7.066	3.999
9	10.195	7.061	3.999
10	10.182	7.056	3.999
11	10.169	7.051	4.000
12	10.157	7.046	4.000
13	10.145	7.042	4.000
14	10.133	7.037	4.001
15	10.121	7.033	4.001
16	10.109	7.029	4.002
17	10.098	7.025	4.002
18	10.086	7.021	4.003
19	10.075	7.017	4.004
20	10.064	7.013	4.005
21	10.054	7.010	4.006
22	10.043	7.006	4.006
23	10.033	7.003	4.007
24	10.023	7.000	4.008
25	10.013	6.997	4.010
26	10.003	6.994	4.011
27	9.994	6.991	4.012
28	9.985	6.989	4.013
29	9.976	6.986	4.015
30	9.967	6.984	4.016
31	9.958	6.981	4.017
32	9.950	6.979	4.019
33	9.941	6.977	4.021
34	9.933	6.976	4.022
35	9.925	6.974	4.024
36	9.918	6.972	4.026
37	9.910	6.971	4.028
38	9.903	6.969	4.029
39	9.896	6.968	4.031
40	9.889	6.967	4.033
41	9.883	6.966	4.035
42	9.876	6.965	4.038
43	9.870	6.965	4.040
44	9.864	6.964	4.042
45	9.858	6.964	4.044
46	9.852	6.963	4.047
47	9.847	6.963	4.049
48	9.842	6.963	4.052
49	9.837	6.963	4.054
50	9.832	6.963	4.057
51	9.827	6.964	4.059
52	9.823	6.964	4.062
53	9.818	6.965	4.065
54	9.814	6.966	4.068
55	9.811	6.966	4.071
56	9.807	6.967	4.074
57	9.804	6.968	4.077
58	9.800	6.970	4.080
59	9.797	6.971	4.083
60	9.794	6.973	4.086
61	9.792	6.974	4.089
62	9.789	6.976	4.093
63	9.787	6.978	4.096
64	9.785	6.980	4.100
65	9.783	6.982	4.103
66	9.782	6.984	4.107
67	9.780	6.987	4.110
68	9.779	6.989	4.114
69	9.778	6.992	4.118
70	9.777	6.995	4.122
71	9.777	6.998	4.126
72	9.776	7.001	4.129
73	9.776	7.004	4.133
74	9.776	7.007	4.138
75	9.776	7.011	4.142
76	9.777	7.014	4.146
77	9.777	7.018	4.150
78	9.778	7.022	4.154
79	9.779	7.026	4.159
80	9.780	7.030	4.163
81	9.782	7.034	4.168
82	9.783	7.039	4.172
83	9.785	7.043	4.177
84	9.787	7.048	4.181
85	9.789	7.052	4.186
86	9.792	7.057	4.191
87	9.794	7.062	4.196
88	9.797	7.067	4.201
89	9.800	7.073	4.206
90	9.803	7.078	4.211
91	9.807	7.084	4.216
92	9.810	7.089	4.221
93	9.814	7.095	4.226
94	9.818	7.101	4.231
95	9.822	7.107	4.237
96	9.827	7.113	4.242
97	9.831	7.120	4.247
98	9.836	7.126	4.253
99	9.841	7.133	4.258
100	9.846	7.139	4.264

Sample Measurement

1. Allow all of the samples to reach the same temperature, since pH readings are temperature dependant. If the samples are not at 25 °C, temperature compensation is recommended. Measure the temperature of the samples using a NIST traceable thermometer and manually enter the temperature into the meter or use an ATC probe to automatically transmit the temperature of the samples to the meter.
2. Prepare the samples as described in the Sample Preparation section and uncover the sample beakers.
3. Rinse the pH electrode first with deionized water and then in the first sample rinse beaker. Make sure to rinse the electrode with deionized water over a waste beaker to prevent contamination of the samples. The electrode should never be rinsed in the same beaker that will be used for sample measurement.
4. Place the electrode into the first sample measurement beaker, so the electrode tip and junction are fully immersed in the sample, and stir the sample at a moderate, uniform rate.
5. Start the measurement on the meter.
6. Wait for a stable reading in the sample, at least 1 to 2 minutes, and then record the pH and temperature of the sample.
7. Repeat steps 3 through 6 for additional samples. Immerse the electrode to the same depth in each sample to obtain the most reproducible sample measurements. When all of the samples have been measured, rinse the electrode with deionized water and store the electrode in pH electrode storage solution.

pH Calibration and Measurement Recommendations

- Check the pH electrode slope daily by performing at least a two buffer calibration. The slope should be 92 to 102% (54.43 to 60.34 mV per pH unit).
- Always pour fresh pH buffers into clean beakers for calibration. Choose buffers that are one to three pH units apart.
- Allow all of the buffers and samples to reach the same temperature, since pH readings are temperature dependant. If the buffers and samples are not at 25 °C, temperature compensation is recommended. Measure the temperature of the buffers and samples using a NIST traceable thermometer and manually enter the temperature into the meter or use an ATC probe to automatically transmit the temperature of the buffers and samples to the meter.
- Since pH readings are temperature dependant and the pH value of each sample will respond differently when the temperature of the sample changes, record the pH of your sample at the same temperature each time for the most accurate, reproducible and comparable results.
- If the electrode is refillable, uncover the fill hole during calibration and measurement to ensure a uniform flow of filling solution. The filling solution level inside of the electrode must be at least one inch above the buffer or sample level.
- The buffer or sample level must be above the pH electrode reference junction when the electrode is immersed in the solution.
- Between buffers or samples, rinse the electrode with deionized water and then with the next buffer or sample. To reduce the chance of errors due to polarization, avoid rubbing or wiping the electrode bulb.
- Use a magnetic stir plate and stir bar or the Thermo Scientific Orion stirrer probe, Cat. No. 096019, to stir all buffers and samples at a moderate, uniform rate. The stirrer probe can be used with the 3-Star, 4-Star and 5-Star benchtop meters and the Orion DUAL STAR™ meter.
- If the application prevents samples from being stirred, for example when small volume samples are measured, do not stir any of the buffers or samples. Keeping the sample and buffer measurement conditions the same will give the best results.
- Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stir plate and beaker to prevent errors from the transfer of heat to the solution.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com/contactwater.

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