

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

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.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

©2009 Thermo Fisher Scientific Inc. All rights reserved. All trademarks are the property of Thermo Fisher Scientific Inc. and its subsidiaries. ROSS and the COIL trade dress are trademarks of Thermo Fisher Scientific Inc. US Patent 6,793,787.



Water Analysis Instruments

North America

166 Cummings Center
Beverly, MA 01915 USA
Toll Free: 1-800-225-1480
Tel: 1-978-232-6000
Dom. Fax: 1-978-232-6015
Int'l Fax: 978-232-6031

Europe

P.O. Box 254, 3860 AG Nijkerk
Wallerstraat 125K, 3862 CN
Nijkerk, Netherlands
Tel: (31) 033-2463887
Fax: (31) 033-2460832

Asia Pacific

Blk 55, Ayer Rajah Crescent
#04-16/24, Singapore 139949
Tel: 65-6778-6876
Fax: 65-6773-0836

www.thermo.com/water

T-PHCAL-E 0808 RevA

Thermo
SCIENTIFIC