

User Guide

*Determination of pH in wastewater by
pH electrode measurement*



Orion Pro Star PH211

UG-004PHWW-E Rev 02 0125

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Introduction

According to Standard Methods for the Examination of Water and Wastewater, pH measurements are one of the most important and frequently used tests in water chemistry.¹ Many biological and chemical reactions are affected by pH; therefore, multiple types of wastewater treatment processes are pH dependent. Monitoring and control of pH is important for pH neutralization, aerobic and anaerobic biological treatment, disinfection by chlorination, pathogen control for sludges, enhanced biological nutrient removal, precipitation reactions, and other treatment processes.

Routine pH testing is utilized for process control during treatment and for compliance monitoring of the final effluent. Process control is meant to ensure that when the final effluent leaves the treatment plant, the water quality meets the regulatory permit requirements. Testing may be conducted at various stages of treatment such as at the influent, primary clarifier, biological treatment, secondary clarifier, and/or final effluent.

Key words

pH in wastewater, primary effluent, secondary effluent, NPDES permit, Orion pH, Orion 8107BNUMD, Orion 8157BNUMD, Standard Methods 4500-H+, ASTM D1293, EPA 150.1, ISO 10523, GB/T 5750.4, IS 3025 (Part 110), proficiency testing, DMRQA, pH QC standard, 40 CFR Part 136.

Equipment

- Thermo Scientific™ Orion™ pH bench meter
- Thermo Scientific™ Orion™ ROSS™ pH/ATC Triode™ (with built-in temperature sensor) - 8157BNUWP (refillable) or 8107BNUMD (low maintenance) recommended
- Thermo Scientific™ Orion™ stirrer probe or a magnetic stirrer with stir bars
- 50 and 100 mL beakers
- Laboratory timer
- Laboratory wipes
- Laboratory wash bottle filled with reagent grade water

Required solutions

- Thermo Scientific™ Orion™ pH buffers: pH 4.01, pH 7.00, and pH 10.01.
- Thermo Scientific™ Orion™ optional pH buffers: 6.86 and/or pH 9.18 (for calibration verification)
- Thermo Scientific™ Orion™ pH electrode filling solution for ROSS™ electrodes
- Thermo Scientific™ Orion™ ROSS™ pH electrode storage solution
- Reagent grade water (RGW)

Electrode setup

See the electrode user manual for the first time preparation of the electrode. See Table 3 Best practices for pH electrodes of this document for a summary of daily, monthly, and as-needed care for the electrode

Meter setup

1. Connect the pH electrode to the BNC connector on the meter.
2. Connect the temperature connector of the pH electrode cable to the ATC connector on the meter.
3. Connect the stirrer probe to the meter.
 - a. If not using the stirrer probe, use a magnetic stirrer and a stir bar to stir each standard and sample. Stirring is required for the fastest response and best method performance.
4. Power up the meter, open the Main Menu / Settings / Instrument Settings, and set the Read Type to Continuous. Save.
5. In Main Menu / Settings, select pH Settings. Set pH Resolution to 0.01 pH, pH Buffer Set to USA, pH Buffer Points to 3, Stirrer to On and Medium speed (if using the stirrer probe), and Slope Type to Segmented. Select Slope Guidance. Set Excellent to 95 to 101%. Set Fair Low Value Range to 92 to 95 and Fair High Value Range to 101 to 102. Set Bad Lowest Value to 92 and Highest Value to 102.
6. Select Create Method and type in the desired method name. Save and Load the method.

Temperature is an important factor when testing pH. The temperature affects the calibration of the pH electrode and can change the pH of the water itself. Using a Triode (having an integrated temperature sensor) is a convenient way to measure temperature and automatically adjust the pH slope to help keep the pH electrode in calibration. When possible, test the pH of your water samples at a consistent temperature to ensure readings are comparable. If using a pH electrode without an integrated temperature sensor, connect a separate automatic temperature compensation (ATC) probe to the meter and place the ATC in the sample with the pH electrode.

User prepared solutions

- Short Term Storage Solution: Pour 25 mL of the pH 7.00 buffer into a 50 mL beaker. Label as “short term storage”. Pour fresh daily. Using this solution for storage during the day can speed up the testing, reduce drift, and improve precision and accuracy.

Calibration

1. Prior to calibration, condition the pH electrode in the short-term storage solution for about 5 minutes.
2. Prepare the pH buffer standards for testing as follows: for each standard, pour 50 mL of buffer into a clean dry 100 mL beaker.
 - a. It is recommended to calibrate at pH 4, 7, and 10. The pH 6.86 and/or 9.18 buffer standards can be used for an independent calibration verification (calibration check standard) after calibration and/or throughout the day.
3. Check that your saved pH of wastewater method name is displayed on the Measurement screen. If not, load the method. From the Main Menu, select Methods, and tap the Play icon to load the method of choice.
4. Select Calibrate to begin the calibration. Perform a three point calibration using the pH 4.0, 7.00, and 10.01 pH buffer standards.
 - a. Rinse the electrode and stirrer probe with generous amounts of RGW from the wash bottle before and after each pH buffer standard reading. Gently shake to remove excess water drops. Blot lightly and gently, if desired. Do not wipe the glass bulb or touch with fingers or hands.
 - b. Lower the electrode and the stirrer probe into the pH 4.01 pH calibration buffer so that about 1 inch of the electrode and stirrer is immersed.
 - c. Select Start (or Continue) to proceed. If the stirrer probe is connected, it will start automatically. Otherwise, turn on the magnetic stir plate.
 - d. Start a 1 minute timer. Allow at least 1 minute for the pH standard buffer to reach a stable reading.
 - i. To ensure good results, it is important to wait at least 1 minute for a truly stable calibration point. Do not rush the calibration. A pH electrode in good working order will typically take from 1 – 2 minutes to stabilize fully.
 - e. After at least 1 minute and when the pH buffer standard reading becomes stable, the meter will automatically display the correct pH buffer value for the recognized standard at the measured temperature.
 - f. Select Next to accept the value and proceed to the next calibration point (or Done after all three pH buffer standards are measured).
 - g. Repeat steps a. through f. for the pH 7.00 and pH 10.01 pH buffer standards, tapping Continue in step c. to proceed.
5. After calibrating with the three standards, select Done to finish the calibration. The calibration is automatically logged into the meter.
 - a. The calibration slopes will be displayed. The slopes of a well-functioning pH electrode properly calibrated with fresh, unexpired buffers will generally be between 95 and 101%.
 - b. A slope between 92 and 102% (but not between 95 to 101%) indicates the need for electrode maintenance and the possibility that the buffers are no longer good.
 - c. If the slopes from pH 4 to 7 and from pH 7 to 10 differ more than 3%, then discard the buffers and pour fresh buffers for calibration. It may be necessary to open a new pH 10 buffer to improve the pH 7 to 10 slope.
 - d. A slope that is not between 92 and 102% is not acceptable. Do not proceed until an acceptable slope is achieved. See the Performance Check section below for corrective actions.

6. If the slope is good, return to Measure mode. Rinse as before, then proceed to the calibration verification or to sample testing. If not using immediately, place the pH electrode into short term storage solution until it is needed.
7. Recommended calibration verification: Read the pH 6.86 and/or 9.18 pH buffer standard to verify the calibration. Set a timer and take the reading after 1 minute. If desired, take another reading at 2 minutes to ensure a stable reading has been achieved.
 - a. After a successful calibration of a well-performing electrode with fresh, unexpired buffers, the calibration check standard will read a value close to the expected value at the measured temperature. Consult your quality department for acceptance limits.
 - b. Alternately, a simple calibration check can be done by a read back of one of the calibration buffers (pH 4.01, 7.00, or 10.01) after the calibration is completed to check that it reads as expected.
 - c. See Table 4 pH vs. temperature of standard calibration buffers to determine the expected value of the buffer at the measured temperature.

Measuring a calibration verification buffer standard has benefits. The best buffer standard choice has a pH value that differs from the pH buffers used for calibration. After a calibration, a good reading for the verification standard gives confidence that the pH calibration buffers are not compromised and that the calibration proceeded successfully, as expected.

Throughout the day, a good calibration verification reading indicates that the pH equipment is still in calibration and may not require recalibration. Check with your quality department for calibration verification requirements.

8. If the calibration verification is not acceptable, take corrective actions as follows:
 - a. Review the meter calibration log to verify the calibration proceeded as expected. Confirm that the segment slopes agree within 3% of each other. If there is an issue, check the buffer standards, as noted in the Electrode Performance Check section below.
 - b. Check the electrode for drift, as noted in the Electrode Performance Check below.
 - c. Consult the troubleshooting section of the pH User Manual.
9. It is best to ensure a good calibration verification reading is achieved before proceeding with sample testing.
10. Proceed to sample preparation and analysis after a good calibration and good calibration verification.

Electrode performance check

If the calibration slope is not between 92 and 102%, conduct a performance check.

1. Check the pH buffer standards: Discard any used standards. Check the expiration date on the buffers and discard any that have expired. Check the date the bottle was opened. Opened bottles are subject to cross-contamination, evaporation, oxidation, dust ingress, and/or carbon dioxide absorption, which can impact the integrity of the buffer. The

composition of pH 10 buffers make them sensitive to carbon dioxide absorption. Open a new bottle or pouch of 10 buffer if the pH 4 to 7 and pH 7 to 10 segment slopes do not agree within 3% or if bottle has been open for more than 6 months or has not been stored properly.

2. Check the electrode: Rinse well, and place the electrode in the pH 4.01 buffer. Stir. Take a mV reading at 1, 2, and 3 minutes. The 2 minute mV reading should be between 117 and 236 mV and ideally within 1 or 2 mV of the 1 minute reading. If the electrode takes more than 3 minutes to stabilize to 1 or 2 mV/minute or is not within the expected mV range, perform maintenance as described in Table 3 Best practices for pH electrode care. For more information, consult the troubleshooting section of the electrode user manual. If maintenance does not restore the performance, replace the electrode.

The pH electrode determines the performance of the testing. Follow the electrode care and maintenance recommendations in Table 3 to help ensure the fastest, most reliable pH readings and to extend the usable lifetime of the electrode.

Sample preparation

1. In general, samples should be measured for pH as soon as possible after collection.
2. Transfer about 50 mL of a well-mixed sample to a clean, dry 100 mL beaker.
3. The sample is ready for analysis.

Sample analysis

1. Check that your saved pH of wastewater method name is displayed on the Measurement screen. If not, load the method. From the Main Menu, select Methods, and tap the Play icon to load your method.
2. Rinse electrode and stirrer probe with generous amounts of RGW and gently shake to remove excess water drops. Blot lightly and gently, if desired. Do not wipe the glass bulb or touch with fingers.
3. Place all probes in the sample and start stirring.
4. Set the timer for 1 minute and start timing.
5. After 1 minute, record the reading or save the reading by selecting Log/Export. If the pH reading is not as expected, allow another minute (2 minutes total) for a more stable pH reading, then record the pH and temperature results.
 - a. If the sample reading is still not as expected, cross contamination may be an issue. Pour another portion of the sample into a clean dry beaker and transfer the electrode and stirrer probe into the second beaker of sample. Set the timer for 1 minute and repeat the reading.

- b. If the temperature reading at 2 minutes is not within 1.0 °C of the 1 minute reading, the sample temperature is changing. That can cause drift of the pH reading.
6. After the measurement, rinse the electrode and stirrer probe with generous amounts of RGW, and gently shake off excess water drops. Blot lightly and gently, if desired. Do not wipe the glass bulb or touch with fingers.
7. Repeat steps 2 through 6 until all the samples have been measured.
8. For storage between samples or throughout the day, place the electrode(s) into the prepared short-term storage solution.

Post sample analysis

1. When testing is done for the day, rinse the electrode thoroughly with RGW. If necessary, clean the electrode before storage as follows: swirl the pH electrode in 1% warm (not hot) lab detergent solution until clean, then rinse thoroughly with RGW until all traces of detergent are removed.
2. Replace the fill hole cover (if using a refillable electrode) and place the electrode into the pH electrode storage solution.
3. Discard used pH buffer standards at the end of the day. Do not pour standards back into the bottle or save for reuse. Reusing standards can lead to alteration and/or contamination of the standard, which can cause incorrect readings.

Quality control (QC)

Recommended QC procedures may include: calibration verification (described above); analysis of a prepared or purchased QC sample; and/or sample duplicates. Consult your Standard Operating Procedures (SOPs) or your quality department for requirements.

pH Testing performance demonstration

A proficiency testing quality control certified reference material standard (QC CRM) was analyzed to demonstrate the Orion pH method for testing pH in wastewater. The QC CRM standard is formulated in a suitable matrix and at a suitable pH level for water pollution (WP) testing and was purchased from an ISO 17034 certified reference material provider.²

Certified laboratories will typically participate in proficiency testing studies one or more times a year. Testing results within the study acceptance limits are generally needed for these laboratories to maintain their certification.

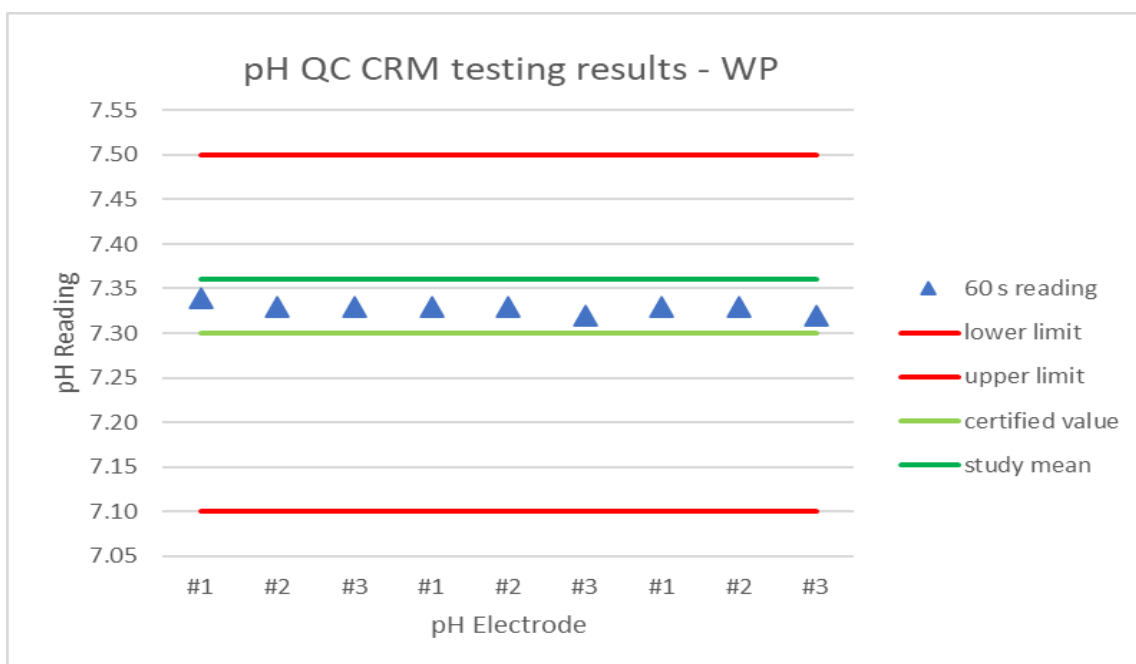
- Two Orion™ ROSS Ultra™ 8157BNUMD refillable pH/ATC Triodes™ and one Orion™ ROSS Ultra™ 8107BNUMD low maintenance pH/ATC Triode™ were used to test the pH QC CRM standard.

- Three replicates of the QC CRM were tested on the three electrodes noted above for a total of 9 measurements (n = 9).
- Reproducibility is good and the measured pH values recorded at 60 seconds are close to the certified concentration.
- All pH test results are well within the acceptance limits of the certificate of analysis.
- The analysis of pH in the QC CRM following this application note indicates the suitability of the noted Orion electrodes, meters, and solutions for this application.

Table 1. pH QC CRM for wastewater testing results - WP			
QC Parameter	pH results*	Certified concentration	Study mean concentration
Average (n = 9)	7.33 ✓	7.30	7.36
Standard deviation	0.01 ✓	Acceptance limits	7.10 – 7.50

*measured at 60 seconds

Figure 1.



Wastewater sample testing results

One 8107BNUMD and two 8157BNUMD electrodes were used to test synthetic wastewaters formulated to replicate primary and secondary effluents³. The calibration slopes were good, and the calibration verification readings were close to the expected values. The wastewater pH readings showed good repeatability and close agreement between the readings on the three electrodes. Standard deviations amongst replicate sample tests were all within +/- 0.04 pH or better. Results are shown in Table 2.

Table 2. Performance of Orion pH electrodes in wastewaters				
Calibration				
Average calibration slope			98.4% ✓	
Calibration Verification				
	pH measured*	Temperature, °C	Expected buffer pH	Difference from expected
Before testing	6.88	20.6	6.88	0.00 ✓
During testing	9.24	20.7	9.22	0.02 ✓
After testing	7.04	20.6	7.01	0.03 ✓
Wastewater testing				
	Primary effluent	Secondary effluent 1*	Secondary effluent 2**	
N = # of readings	9	15	15	
Average pH*	7.32	7.82	7.83	
Standard deviation	0.02 ✓	0.04 ✓	0.02 ✓	
Temp, °C	20.4	20.5	20.5	

*average of readings, all measured at 60 seconds. **average of readings, all measured at 90 seconds.

Hints and tips for pH testing in wastewater

- Refer to the electrode user manual for details on cleaning, storage, and maintenance recommendations to keep the electrode performing well. Main points for electrode care are summarized below in Table 3 Best practices for pH electrode care.
- Conditioning the electrode in a portion of a pH buffer standard for a few minutes before calibration will speed up the calibration and improve stability and accuracy. Short-term storage in this solution during the day will also speed up sample results and improve precision and accuracy.
- Use a timer and allow at least 1 minute wait time before accepting a pH measurement. This applies to the calibration and to testing water samples. If the reading has not stabilized or is not as expected, wait another minute. Don't rush the calibration or the sample readings. It is worth the extra minute, and your results will be better for it.
- After calibration, it is important to rinse the electrode and stirrer very thoroughly to remove all traces of buffer. A small amount of buffer carried over into a clean water sample (such as a secondary effluent) may change the pH of the sample you are trying to measure.
- Good quality wastewater effluents are clean water samples. If faster or more consistent pH readings are desired, consider rinsing the electrode with a portion of your clean water sample prior to testing. This step is done after the RGW rinse, but before placing the electrodes into the poured sample. For example, fill two beakers with the same water sample. After the RGW rinse, swirl the electrode in the first beaker for 10 seconds and allow to sit for 1 minute. Then place the electrode directly into the second beaker (no rinse between) and start the timer for your 1 minute wait time. Proceed as recommended in the Sample analysis section above.
- pH standards are meant to be poured fresh each day of testing. Discard used standards at the end of the day. Do not pour standards back into the bottle or save for reuse. Reusing standards can lead to alteration and/or contamination of the standard, which can cause incorrect readings.

Electrode care

Refer to the electrode user manual for details on cleaning, storage, and maintenance recommendations to keep the electrode performing well. Main points for care are summarized below.

Table 3: Best practices for pH electrode care

Daily Care	Monthly Care	As Needed
<ul style="list-style-type: none"> • If refillable, open the fill hole cover and top up the appropriate electrode filling solution to the bottom of the fill hole. Leave the fill hole cover off during testing. • Prepare short term storage solution by pouring 25 mL of the pH 7.00 buffer into a 50 mL beaker. • Before and after each pH reading, rinse with generous amounts of RGW. Also direct the spray between the protective prongs to wash the bulb, junction, and thermistor. • After testing, store the clean electrode in the pH electrode storage solution. If refillable, replace the fill hole cover prior to storage. 	<ul style="list-style-type: none"> • If refillable, drain the fill solution and rinse the chamber with RGW*. Replace the electrode filling solution. • Discard the used overnight storage solution. Use fresh solution. • If electrode becomes drift or slow, soak 15 minutes in warm (not hot) 1% laboratory detergent. Rinse thoroughly, drain the fill solution, and refill (if refillable), then store in overnight pH electrode storage solution, as usual. 	<ul style="list-style-type: none"> • For long term storage (more than 1 or 2 weeks), follow the instructions in the pH electrode user manual. • If crystals form inside a refillable electrode or the fill solution becomes discolored, drain the fill solution. Then rinse the chamber until crystals or discoloration are gone. Replace the filling solution. • See the user manual for more maintenance details.

*- See the electrode user manual for details on all electrode care procedures.

Table 4. pH vs. temperature of standard calibration buffers

pH Buffers	15°C	20°C	25°C	30°C	35°C
pH 4.01 buffer value	4.00	4.00	4.01	4.02	4.02
pH 6.86 buffer value	6.90	6.88	6.86	6.85	6.84
pH 7.00 buffer value	7.03	7.01	7.00	6.98	6.97
pH 9.18 buffer value	9.28	9.23	9.18	9.14	9.11
pH 10.01 buffer value	10.12	10.06	10.01	9.97	9.93

Ordering information

Product	Description	Cat. No.
Meter Kit options	Orion Pro Star PH211 pH/ORP Bench Meter Durable Kit with 8157BNUWP pH/ATC Triode	PSTAR2116
	Orion Pro Star PH211 pH/ORP bench meter low maintenance kit with 8107BNUMD pH/ATC Triode	PSTAR2117
Accessories	Orion stirrer probe	096019-WA
Solutions	Orion pH 4.01 buffer standard	910104
	Orion pH 7.00 buffer standard	910107
	Orion pH 10.01 buffer standard	910110
	Orion pH 6.86 buffer standard (optional)	910686
	Orion pH 9.18 buffer standard (optional)	910918
	Orion ROSS electrode filling solution (for 8157BNUMD electrode)	810007
	Orion ROSS pH electrode storage solution	810001
Laboratory Grade Water	Thermo Scientific Barnstead Smart2Pure 12 UV Water Purification System	50129890*

*Please contact your local Thermo Scientific™ representative for support to order a suitable water purification system for your application.

References

- 1) Standard Methods for the Examination of Water and Wastewater, 4500-H⁺ pH Value, American Public Health Association (APHA), American Water Works Association (AWWA), Water Environment Federation (WEF), 24th edition, 2023.
- 2) NSI Lab Solutions, QCI-035 pH QC CRM, lot N0124. Certified date: December 26, 2023.
- 3) Kargol AK, Burrell SR, Chakraborty I, Gough HL (2023) Synthetic wastewater prepared from readily available materials: Characteristics and economics. PLOS Water 2(9): e0000178. <https://doi.org/10.1371/journal.pwat.0000178>.

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