

User Guide

Green pH
Electrodes



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This publication supersedes all previous publications on this subject.

Table of Content

Introduction	1
Required Equipment	2
Electrode Preparation	3
Green Gel-filled pH Electrode Preparation	3
Green Refillable pH Electrode Preparation	3
Electrode Calibration	4
General Calibration Procedure	4
One Buffer Calibration	4
Two Buffer Calibration	5
Sample Requirements	6
Measuring Hints	6
pH Measurement	7
Electrode Storage	7
Electrode Maintenance	8
General Cleaning	8
Cleaning Solutions	8
Electrode Characteristics	9
Temperature Effects	9
Interferences	10
Troubleshooting	11
Assistance	12
Warranty	12
Ordering Information	13
Specifications	14

Introduction

This user guide contains information on the preparation, operation and maintenance of the Thermo Scientific Orion Green pH electrodes.

The Thermo Scientific Orion Green pH electrodes contain no lead, mercury or other hazardous substance, which makes these electrodes environmentally friendly and allows for easy and hassle-free electrode disposal. The Green electrodes are the first laboratory glass-bulb pH electrodes to meet all the requirements of RoHS. Other glass-bulb pH electrodes are manufactured with glass that contains about 20% lead. Currently, pH electrodes have an exemption from RoHS because of the lead content. We have taken the initiative and removed lead from the Green pH electrodes.

- The GS9106BNWP and GD9106BNWP electrodes are low maintenance and contain a gel that does not need to be refilled.
- The GS9156BNWP and GD9156BNWP electrodes are refillable for easy electrode cleaning and maintenance.
- The GD9106BNWP and GD9156BNWP electrodes are double junction, so they can be used in samples that contain silver-complexing or binding agents such as TRIS buffer, proteins and sulfides.

Cat. No.	Description
GS9106BNWP	Green gel-filled single junction combination pH electrode with epoxy body and waterproof BNC connector
GD9106BNWP	Green gel-filled double junction combination pH electrode with epoxy body and waterproof BNC connector
GS9156BNWP	Green refillable single junction combination pH electrode with epoxy body and waterproof BNC connector
GD9156BNWP	Green refillable double junction combination pH electrode with epoxy body and waterproof BNC connector

Required Equipment

1. Thermo Scientific Orion pH meter, such as the 3-Star pH meter, 4-Star pH/ISE meter, 4-Star pH/DO meter, 4-Star pH/conductivity meter or 5-Star pH/ISE/DO/conductivity meter.

Green pH electrodes can be used on any pH meter with a BNC connection. These electrodes can also be used on meters with a variety of inputs when an adapter cable is used. Visit www.thermo.com/water for details.

2. Thermo Scientific Orion Green pH electrode.
3. The GS9156BNWP electrode requires single junction electrode filling solution, Cat. No. 900011. The GD9156BNWP electrode requires double junction electrode filling solution, Cat. No. 910008.
4. pH electrode storage solution, Cat. No. 910001. If pH electrode storage solution is not available, a temporary storage solution can be prepared by adding about 1 gram of potassium chloride (KCl) to 200 mL of pH 7 buffer.
5. pH buffers. At least two pH buffers are recommended for precise measurements. One buffer should be near pH 7 and buffers should be one to three pH units apart.
6. Beakers, plastic or glass.
7. Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.
8. Distilled or deionized water.

Electrode Preparation

Green Gel-filled pH Electrode Preparation – GS9106BNWP and GD9106BNWP

1. Remove the storage bottle from the electrode and save the bottle for later storage.
2. Clean any salt deposits from the exterior of the electrode by rinsing it with distilled water.
3. Connect the electrode to the meter.
4. If the electrode will not be used immediately, soak it in pH electrode storage solution, Cat. No. 910001.

Green Refillable pH Electrode Preparation – GS9156BNWP and GD9156BNWP

1. Remove the storage bottle from the electrode and save the bottle for later storage.
2. Clean any salt deposits from the exterior of the electrode by rinsing with distilled water.
3. Uncover the filling hole by removing the tape and add electrode filling solution to the electrode up to the fill hole. Add Cat. No. 900011 to the GS9156BNWP electrode. Add Cat. No. 910008 to the GD9156BNWP electrode.

To maintain an adequate flow rate, the level of filling solution must always be above the reference junction and at least one inch above the sample level. The filling hole should be open whenever the electrode is in use.

4. Shake the electrode downward (similar to a clinical thermometer) to remove any air bubbles.
6. Connect the electrode to the meter.
6. If the electrode will not be used immediately, soak it in pH electrode storage solution, Cat. No. 910001.

Electrode Calibration

General Calibration Procedure

For detailed instructions on pH calibration and temperature compensation, consult the meter user guide.

One Buffer Calibration

1. Choose a buffer near expected sample pH.
2. The buffer should be at same temperature as the sample. If the buffer and samples are at varying temperatures, temperature compensation is recommended.
3. Prepare the meter according to the meter user guide.
4. Rinse the electrode first with distilled water and then with the buffer being used for calibration.
5. Place the electrode into the buffer. When the reading is stable, set the meter to the pH value of the buffer at the measured temperature. Refer to the meter user guide for a detailed procedure. **Table 1** provides the pH values for Thermo Scientific Orion buffers at various temperatures.
6. Proceed to the **pH Measurement** section.

Table 1
pH Values of Buffers at Various Temperatures

Nominal pH Value at 25 °C	Temperature				
	0 °C	5 °C	10 °C	20 °C	30 °C
1.68	1.67	1.67	1.67	1.67	1.68
3.78	3.86	3.84	3.82	3.79	3.77
4.01	4.00	4.00	4.00	4.00	4.02
6.86	6.98	6.95	6.92	6.87	6.85
7.00	7.11	7.08	7.06	7.01	6.98
7.41	7.53	7.50	7.47	7.43	7.40
9.18	9.46	9.40	9.33	9.23	9.14
10.01	10.32	10.25	10.18	10.06	9.97

Two Buffer Calibration

This procedure is recommended for precise measurements.

1. Select two buffers that bracket the expected sample pH. The first buffer should be near the electrode isopotential point (pH 7) and the second should be near the expected sample pH (pH 4 or pH 10).
2. The buffers should be at same temperature as the sample. If the buffers and samples are at varying temperatures, temperature compensation is recommended.
3. Rinse the electrode first with distilled water and then with the first buffer.
4. Place the electrode into the first buffer. When the reading is stable, set the meter to the pH value of the buffer at the measured temperature. Refer to the meter user guide for a detailed procedure. **Table 1** provides the pH values for Thermo Scientific Orion buffers at various temperatures.
5. Rinse the electrode first with distilled water and then with the second buffer.
6. Place the electrode into the second buffer. When the reading is stable, set the meter to the pH value of the buffer at the measured temperature. Refer to the meter user guide for a detailed procedure.
7. Proceed to the **pH Measurement** section.

Temperature					
40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
1.69	1.71	1.72	1.74	1.77	1.79
3.75	3.75				
4.04	4.06	4.09	4.13	4.16	4.21
6.84	6.83	6.84	6.85	6.86	6.88
6.97	6.97	6.97	6.99	7.03	7.08
7.38	7.37				
9.07	9.01	8.96	8.92	8.89	8.85
9.89	9.83				

Sample Requirements

The Green pH electrodes have an epoxy body and should not be used in samples that contain non-aqueous solutions or organic solvents.

The Green single junction pH electrodes, Cat. No. GS9106BNWP and GS9156BNWP, contain a silver/silver chloride (Ag/AgCl) reference that is incompatible with solutions that contain silver complexing or binding agents such as TRIS buffer, proteins and sulfides. To measure pH in these solutions, use the Green double junction pH electrodes, Cat. No. GD9106BNWP and GD9156BNWP. Proteins cause the additional problem of coating the sensing bulb, so extra care should be taken to keep the electrode clean while measuring samples.

Measuring Hints

- Always use fresh buffers for calibration. Choose buffers that are one to three pH units apart.
- Check electrode slope daily by performing a two buffer calibration. The slope should be 92 to 102%.
- If using a refillable pH electrode, remove the filling hole cover during measurements to ensure a uniform flow of filling solution.
- Between measurements, rinse electrodes with distilled water and then with the next solution to be measured.
- Stir all buffers and samples at a uniform rate.
- Keep buffers and samples at the same temperature. If samples are at different temperatures, use temperature compensation, as described in the meter user guide.
- Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stirrer and beaker to prevent measurement errors from the transfer of heat to the sample.
- To reduce the chance of error due to polarization, avoid rubbing or wiping the electrode bulb. Use a lint-free tissue and gently blot the bulb.

pH Measurement

1. Calibrate the electrode as described in the **Electrode Calibration** section.
2. Rinse the electrode with distilled water and then with the sample.
3. Place the electrode into the sample.
4. When the reading is stable, record the pH and temperature of the sample.

Electrode Storage

To ensure a quick response and free-flowing junction, the sensing element and reference junction must not dry out.

Short-term Storage (up to one week) – Soak the electrode in pH electrode storage solution, Cat. No. 910001. If using a refillable pH electrode, cover the fill hole whenever the electrode is being stored to prevent crystallization of the filling solution and open the fill hole when calibrating and measuring. Do not store the electrode in distilled or deionized water, as it will shorten the electrode life.

Long-term Storage (more than one week) – Rinse off any salt buildup with distilled water and remove any membrane/junction deposits. If using a refillable pH electrode, fill the reference chamber with the appropriate filling solution and securely cover the fill hole. Add pH electrode storage solution, Cat. No. 910001, to the storage bottle and insert the electrode into the storage bottle. Before returning the electrode to use, prepare it as a new electrode.

Electrode Maintenance

1. Inspect the electrode for scratches, cracks, salt crystal buildup or membrane/junction deposits.
2. Rinse off any salt buildup with distilled water. Remove any membrane/junction deposits as directed in the **General Cleaning** section.
3. If using a refillable pH electrode, drain the reference chamber, flush it with fresh filling solution and refill the chamber with fresh filling solution.

General Cleaning

1. If using a gel-filled pH electrode, soak the electrode in 0.1 M HCl or 0.1 M HNO₃ for 10 to 15 minutes. If using a refillable pH electrode, soak the electrode in 0.1 M HCl or 0.1 M HNO₃ for 15 to 30 minutes.

The electrode can also be soaked for 15 minutes in a 1:10 dilution of household laundry bleach or a 0.1 to 0.5% liquid detergent solution mixed with hot water. The solution should be stirred at a moderate to fast rate.

2. If using a refillable pH electrode, drain the reference chamber and refill it with fresh filling solution.
3. Soak the electrode in pH electrode storage solution for at least one hour.

Cleaning Solutions

Cat. No. 900021– pH cleaning solution A, for removing protein contaminants.

Cat. No. 900022– pH cleaning solution B, for general cleaning and removing bacterial contaminants.

Cat. No. 900023– pH cleaning solution C, for general cleaning.

Cat. No. 900024– pH cleaning solution D for removing oil and grease contaminants.

Cat. No. 900020– pH cleaning solution kit, includes one bottle each of cleaning solutions A, B, C and D.

Electrode Characteristics

Temperature Effects

The most common cause of error in pH measurements is temperature. There are at least five ways that temperature variations can affect pH: electrode slope, buffers, samples, reference element drift and temperature sensor errors

Electrode Slope Changes

The electrode slope will change with variations in temperature. Slope changes may be compensated manually or automatically with an automatic temperature compensation (ATC) probe. Thermo Scientific Orion pH meters calculate the slope based on the measured temperature and automatically adjust the pH value based on the temperature.

Buffer and Sample pH Changes

Buffer and sample pH values change with temperature because of their temperature dependent chemical equilibria. The pH electrode should be calibrated with buffers that have known pH values at different temperatures. Buffer values at different temperatures are given in **Table 1**. Thermo Scientific Orion pH meters automatically calibrate with the correct pH buffer values based on the measured temperature. All pH meters are unable to correct pH values back to a reference temperature because every sample has a unique pH value versus temperature relationship. Therefore, calibration and measurements should be performed at the same temperature and pH values should be reported with temperature.

Reference Element Drift

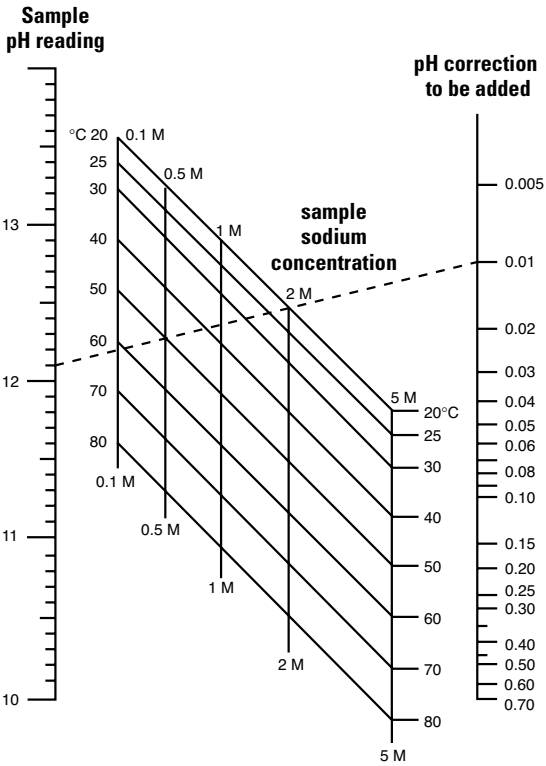
Drift can occur when the internal reference elements inside the pH and reference portions of the electrode are reaching thermal equilibrium after a temperature change. Long-term drift or slow response can last until the sample and electrode are at the same temperature.

Temperature Sensor Errors

When a pH and temperature probe are placed into a sample that varies significantly in temperature, the readings can drift for two reasons. First, the temperature response of the electrode and temperature probe may not be similar, which prolongs equilibration and drift. Second, a sample may not have a uniform temperature. Therefore, the pH electrode and temperature probe are responding to different environments.

Interferences

Sodium ions are the principal interference of the pH electrode and cause increasing error at higher pH (lower hydrogen ion activities) and at higher temperatures. Because the pH membrane is composed of special low sodium error glass, error due to sodium is negligible when measuring at pH values less than 12. When measuring at pH values greater than 12, add the correction value from the nomograph below to the observed pH reading.



Typical Sodium Error

Example:

pH reading	12.10
Sodium concentration	0.5 M
Temperature	50 °C
Correction	0.01
Corrected pH reading	12.11

Troubleshooting

Follow a systematic procedure to isolate the problem. The pH measuring system can be divided into four components for ease in troubleshooting: pH meter, electrode, sample/application and technique.

pH Meter

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion pH meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the pH meter user guide for directions.

Electrode

To test electrode operation:

1. Connect the electrode to a working meter that has a mV measuring mode.
2. Set the meter to the mV measuring mode.
3. Rinse the electrode with distilled water and then insert the electrode into fresh pH 7 buffer.
4. When the reading is stable, record the mV value of the pH 7 buffer. The mV value should be -30 to +30 mV.
5. Rinse the electrode with distilled water and then insert the electrode into fresh pH 4 buffer.
6. When the reading is stable, record the mV value of the pH 4 buffer. The mV value should be +150 to +210 mV.
7. Calculate the absolute mV difference between the two buffers. The mV difference should be 160 to 180 mV. The actual mV values will change as the electrode ages, but the mV difference between the two buffers should always be 160 to 180 mV.

If the electrode fails this procedure, clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Replace the electrode if cleaning and maintenance fail to rejuvenate it.

Sample/Application

The electrode and meter may operate with buffers, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed.

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.

Warranty

For the most current warranty information, visit www.thermo.com/water.

Ordering Information

Cat. No.	Description
GS9106BNWP	Green gel-filled single junction combination pH electrode with epoxy body and waterproof BNC connector
GD9106BNWP	Green gel-filled double junction combination pH electrode with epoxy body and waterproof BNC connector
GS9156BNWP	Green refillable single junction combination pH electrode with epoxy body and waterproof BNC connector
GD9156BNWP	Green refillable double junction combination pH electrode with epoxy body and waterproof BNC connector
900011	Green single junction electrode filling solution, 5 x 60 mL bottles
910008	Green double junction electrode filling solution, 5 x 60 mL bottles
910001	pH electrode storage solution, 475 mL bottle
910003	Electrode storage bottles, 3 pack
900020	pH cleaning solution kit, includes A, B, C and D cleaning solutions, pipette and beaker
910199	All-in-One pH buffer kit, includes 475 mL bottle each of pH 4.01, 7.00 and 10.01 buffers and pH electrode storage solution, and one electrode storage bottle
910168	pH 1.68 buffer, 475 mL bottle
910104	pH 4.01 buffer, 475 mL bottle
910105	pH 5.00 buffer, 475 mL bottle
910686	pH 6.86 buffer, 475 mL bottle
910107	pH 7.00 buffer, 475 mL bottle
910918	pH 9.18 buffer, 475 mL bottle
910110	pH 10.01 buffer, 475 mL bottle
910112	pH 12.46 buffer, 475 mL bottle

Visit www.thermo.com/water for additional pH electrode accessories, buffers and buffer sizes.

Specifications

	GS9106BNWP	GD9106BNWP
pH Range	0 to 14	0 to 14
Temperature Range	0 to 90 °C	0 to 90 °C
pH Precision	0.05	0.02
Reference Type	Ag/AgCl single junction	Ag/AgCl double junction
Junction Material	Glass Fiber	Glass Fiber
Electrode Length	120 mm	120 mm
Electrode Diameter	12 mm	12 mm
Cable Length	1 meter	1 meter
Required Filling Solution	None	None

	GS9156BNWP	GD9156BNWP
pH Range	0 to 14	0 to 14
Temperature Range	0 to 90 °C	0 to 90 °C
pH Precision	0.02	0.02
Reference Type	Ag/AgCl single junction	Ag/AgCl double junction
Junction Material	Glass Fiber	Glass Fiber
Electrode Length	120 mm	120 mm
Electrode Diameter	12 mm	12 mm
Cable Length	1 meter	1 meter
Required Filling Solution	4 M KCl with Ag/AgCl, Cat. No. 900011	3 M KCl Cat. No. 910008

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