

User Guide

Refillable Ag/AgCl
pH Electrodes



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ORION Series A meters and 900A printer are protected by U.S. patents 5,198,093, D334,208 and D346,753.

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ROSS Ultra electrodes are protected by US patents 6,793,787.

Orion ORP Standard is protected by US Patent 6,350,367.

Orion NoCal electrodes with stabilized potential patent pending.

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This publication supersedes all previous publications on this subject.

Introduction

This user guide contains information on the preparation, operation and maintenance of the Thermo Scientific Orion refillable Ag/AgCl (silver/silver chloride) pH electrodes.

All refillable Ag/AgCl pH electrodes have a pH range of 0 to 14 and silver/silver chloride reference system. Refillable Ag/AgCl electrodes have a pH precision of 0.02 or 0.01. The electrodes have a temperature range of 0 to 90 °C or 0 to 100 °C.

Refillable Ag/AgCl Electrodes

Refillable Ag/AgCl pH electrodes include a wide selection of electrode shapes and sizes for measuring a variety of samples. These reliable electrodes are built for everyday use.

Sure-Flow® Refillable Ag/AgCl Electrodes

Sure-Flow electrodes incorporate a free-flowing junction that is easy to clean and never clogs. These electrodes are ideal for dirty or viscous samples that clog traditional electrodes.

PerpHecT® Refillable Ag/AgCl Electrodes

PerpHecT electrodes are designed to be used with PerpHecT meters to provide both pH and temperature measurements. The PerpHecT meters use patented LogR technology that allows temperature to be measured using the resistance of the PerpHecT electrode.

Cat. No.	Description
9101BN / 9101SC	Ag/AgCl pH half-cell electrode with glass body and BNC connector / screw cap connector
9102BNWP / 9102SC	Refillable Ag/AgCl combination pH electrode with glass body and waterproof BNC connector / screw cap connector
9103BNWP / 9103SC	Refillable Ag/AgCl combination pH electrode with glass body, semi-micro tip, and waterproof BNC connector / screw cap connector
9104BNWP / 9104SC	Refillable Ag/AgCl combination pH electrode with glass body, rugged bulb, and waterproof BNC connector / screw cap connector
9156BNWP / 915500 / 9156SC	Refillable Ag/AgCl combination pH electrode with epoxy body and waterproof BNC connector / U.S. standard connector / screw cap connector
9157BNMD	Refillable Ag/AgCl pH/ATC Triode with epoxy body and waterproof BNC and 8 pin MiniDIN connectors
9157BN	Refillable Ag/AgCl pH/ATC Triode with epoxy body and BNC and 8 pin DIN connectors
9161BN / 9161SC	Ag/AgCl pH half-cell electrode with glass body, low resistance bulb, and BNC connector / screw cap connector
9162BNWP / 9162SC	Refillable Ag/AgCl combination pH electrode with glass body, low resistance bulb, and waterproof BNC connector / screw cap connector
9163SC	Refillable Ag/AgCl combination pH electrode with glass body, spear tip and screw cap connector
9164SC	Refillable Ag/AgCl combination pH electrode with glass body, 14/15 standard taper and screw cap connector
9165BNWP	Sure-Flow refillable Ag/AgCl combination pH electrode with epoxy body and waterproof BNC connector
9166SC	Refillable Ag/AgCl combination pH electrode with glass body, sleeve junction and screw cap connector

Cat. No.	Description
9167SC	Refillable Ag/AgCl combination pH electrode with glass body, semi-micro and flat surface tip, and screw cap connector
9172BNWP	Sure-Flow refillable Ag/AgCl combination pH electrode with glass body and waterproof BNC connector
9202BN	PerpHecT refillable Ag/AgCl combination pH electrode with glass body and BNC connector
9203BN	PerpHecT refillable Ag/AgCl combination pH electrode with glass body, semi-micro tip and BNC connector
9256BN	PerpHecT refillable Ag/AgCl combination pH electrode with epoxy body and BNC connector
9272BN	PerpHecT Sure-Flow refillable Ag/AgCl combination pH electrode with glass body and BNC connector

- All electrodes with a waterproof BNC, BNC and U.S. standard connector have one meter cable lengths.
- All electrodes with a screw cap connector require a separate cable.
- Electrodes with a waterproof BNC connector can be used on any pH meter with a BNC connection.
- The 9101BN / 9101SC and 9161BN / 9161SC pH half-cell electrodes can be used with the 900100 single junction reference electrode or 900200 double junction reference electrode.

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.

Refillable Ag/AgCl pH electrodes can be used on any pH meter with a BNC or U.S. standard connection. The 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.

Refillable Ag/AgCl Triodes have temperature connectors that are compatible with specific meters, refer to the list below.

2. Thermo Scientific Orion refillable Ag/AgCl pH electrode.
 - The 9157BNMD pH/ATC Triode has a temperature connector that is compatible with the Star Series pH meters.
 - The 9157BN pH/ATC Triode has a temperature connector that is compatible with the A+ Series meters.
3. Ag/AgCl electrode filling solution, Cat. No. 900011.
4. pH electrode storage solution, Cat. No. 910001.
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 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.

Sample Requirements

Electrodes with an epoxy body should only be used in aqueous solutions.

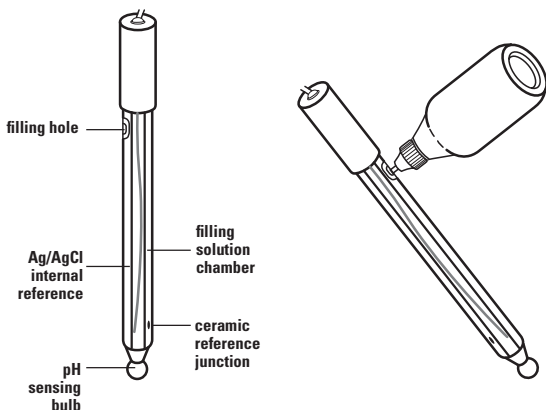
Electrodes with a glass body may be used in non-aqueous solutions and solutions that contain organic solvents. A minimum of 20% water must be present in the sample for the best measurement results. Visit www.thermo.com/water to download Dr. Martin S. Frant's article "How to Measure pH in Mixed and Nonaqueous Solutions" and for additional information on non-aqueous pH measurements.

The refillable Ag/AgCl electrodes contain a silver/silver chloride (Ag/AgCl) reference that may become clogged in solutions that contain silver complexing or binding agents such as TRIS, proteins and sulfides. Frequent cleaning may be required when measuring solutions that contain these agents. Proteins cause the additional problem of coating the sensing bulb, so extra care should be taken to keep the electrode clean while measuring samples that contain proteins.

Electrode Preparation

Electrode Preparation for Non-Sure-Flow® Models

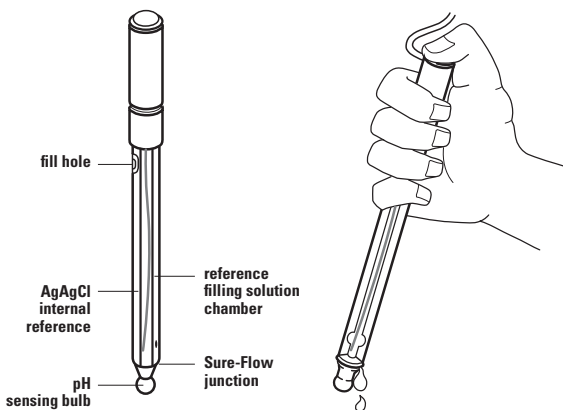
1. Remove the protective shipping cap from the sensing element and save the cap for storage.
2. Clean any salt deposits from the exterior of the electrode by rinsing with distilled water.
3. Uncover the filling hole by removing the tape and then add electrode filling solution, Cat. No. 900011, to the 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. Place the electrode in an electrode holder and suspend the electrode in air for 5 minutes to thoroughly wet the reference junction.
5. Shake the electrode downward (similar to a clinical thermometer) to remove air bubbles.
6. Soak electrode in pH electrode storage solution, Cat. No. 910001, for 30 to 60 minutes.
7. Connect the electrode to the meter.



Refillable Ag/AgCl Combination pH Electrode

Electrode Preparation for Sure-Flow® Models

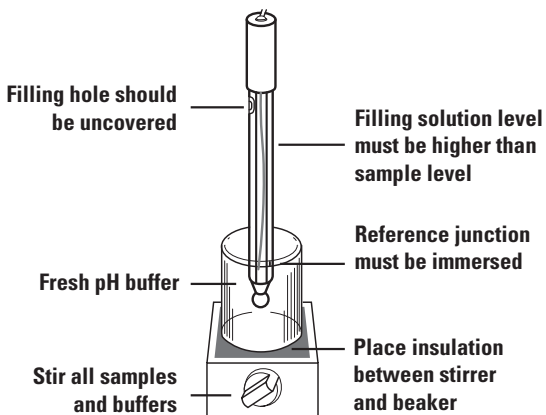
1. Remove the protective shipping cap from the sensing element and save the cap for storage.
2. Clean any salt deposits from the exterior of the electrode by rinsing with distilled water.
3. Uncover the filling hole by removing the tape and then add electrode filling solution, Cat. No. 900011, to the 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. Wet the junction by pressing down on the electrode cap to let a few drops of the filling solution flow out of the electrode and then replenish any lost solution.
5. Shake the electrode downward (similar to a clinical thermometer) to remove air bubbles.
6. Soak electrode in pH electrode storage solution, Cat. No. 910001, for 30 to 60 minutes.
7. Connect the electrode to the meter.



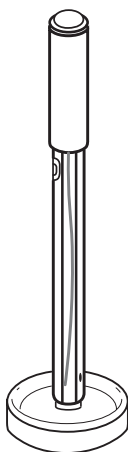
Sure-Flow Refillable Ag/AgCl Combination pH Electrode

Measuring Hints

- Always use fresh buffers for calibration. Choose buffers that are one to three pH units apart.
- Check the electrode slope daily by performing a two buffer calibration. The slope should be 92 to 102%.
- 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.
- 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 electrode bulb.
- If the electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely and hold the junction under running water. Empty any water from the electrode and refill it with fresh electrode filling solution.
- If a Sure-Flow electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely and hold the junction open under running water. Empty any water from the electrode and refill it with fresh electrode filling solution. Press down on the electrode cap to let a few drops of the filling solution flow out of the electrode and then replenish any lost solution.
- Flat surface electrodes may be used on any moist surface or in liquids.



Measuring Hints



Using a Flat Surface Electrode

Electrode Calibration

General Calibration Procedure

For detailed instructions on pH calibration, manual pH calibration and temperature compensation, consult your meter user guide. When using PerpHecT electrodes with a PerpHecT pH meter, refer to the PerpHecT meter user guide for instructions on temperature calibration and LogR temperature compensated pH measurements.

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 pH values at various temperatures.
6. Proceed to the **pH Measurement** section.

Table 1
pH Values of Buffers at Various Temperatures

Nominal Buffer Value at 25°C	Temperature				
	0 °	5 °	10 °	20 °	30 °
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 pH values 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. **Table 1** provides pH values at various temperatures.
7. Proceed to the **pH Measurement** section.

Temperature					
40 °	50 °	60 °	70 °	80 °	90 °
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				

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. To prevent crystallization of the fill solution, cover the fill hole whenever the electrode is being stored and open the fill hole when calibrating and measuring.

Long-term Storage (more than one week)

Fill the reference chamber and securely cover the filling hole. Cover the sensing element and reference junction with the protective cap/sleeve containing a few drops of storage solution. 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. Drain the reference chamber, flush it with fresh filling solution and refill the chamber with fresh filling solution.

Electrode Cleaning Procedures

General Cleaning

1. Soak the electrode in 0.1 M HCl or HNO₃ for half an hour.

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. 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 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 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, automatically with an automatic temperature compensation (ATC) probe or with LogR technology when using a PerpHecT meter and electrode. 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 vs. 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.

Using LogR technology, PerpHecT meters sense the temperature directly from the PerpHecT pH electrodes. The pH and temperature response is identical and both measurements occur at the sensing bulb. Drift is minimized and errors due to environmental differences are eliminated.

Sure-Flow® Electrode Leak Rate

The junction of the Sure-Flow electrodes has been designed to leak at a rate of approximately 1 mL per 24 hours. To keep the junction from clogging, the leak rate is slightly higher than conventional electrodes. During the average pH measurement time the loss of filling solution is minimal and the filling solution does not contaminate the sample.

PerpHecT® Electrode Operation with PerpHecT® pH Meters

When PerpHecT electrodes are used with a PerpHecT pH meter, enhanced temperature compensation is achieved without the need of a separate ATC probe. Using LogR technology, the temperature of the solution is measured through the resistance of the pH electrode. PerpHecT pH electrodes are manufactured to meet the PerpHecT meter specifications, so optimum performance and accuracy are achieved in LogR mode.

Each PerpHecT pH electrode must be calibrated for temperature before a pH measurement is performed using LogR technology. Refer to the PerpHecT meter user guide for details. For maximum precision, a three point temperature calibration is recommended. Do not perform a one point temperature calibration if measured solutions will be below 20 °C. The following tables illustrate the expected pH compensation error for one, two and three point temperature calibrations. The accuracy values are valid only when the temperature calibration is performed within the stated temperature range. The higher temperature range data will apply to measurements made above that temperature range, provided that calibration points are within 20 °C of each other. When highly accurate pH results are desired, a separate ATC probe is recommended.

One Point Temperature Calibration

Electrode	Average temp. error 20-30 °C	Average temp. error 30-50 °C	Average pH error 20-30 °C	Average pH error 30-50 °C
9202BN	0.26	0.17	0.003	0.002
9203BN	0.12	0.21	0.001	0.003
9256BN	0.22	0.12	0.003	0.001
9272BN	0.08	0.11	0.001	0.001

Two Point Temperature Calibration

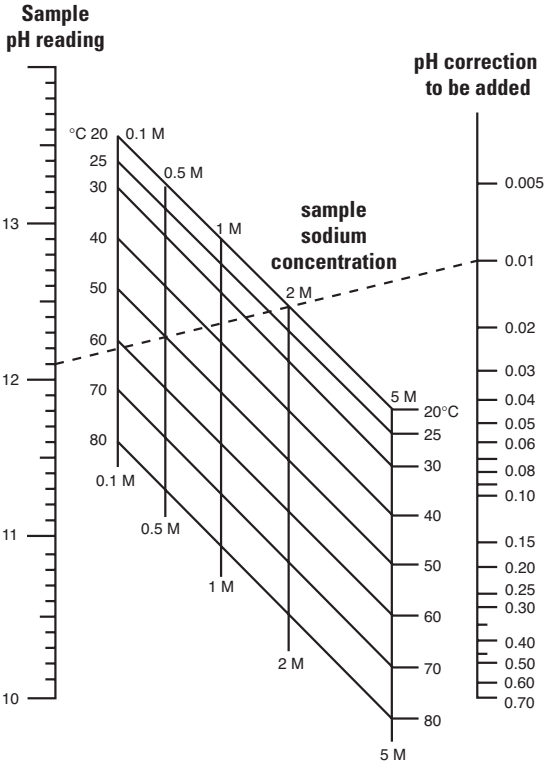
Electrode	Average temp. error 0-25 °C	Average temp. error 20-40 °C	Average pH error 0-25 °C	Average pH error 20-40 °C
9202BN	0.21	0.06	0.003	0.001
9203BN	0.20	0.10	0.002	0.001
9256BN	0.27	0.07	0.003	0.001
9272BN	0.22	0.06	0.003	0.001

Three Point Temperature Calibration

Electrode	Average temp. error 0-25 °C	Average temp. error 20-40 °C	Average. pH error 0-25 °C	Average. pH error 20-40 °C
9202BN	0.02	0.04	0.000	0.000
9203BN	0.03	0.06	0.000	0.001
9256BN	0.07	0.07	0.001	0.001
9272BN	0.02	0.00	0.000	0.000

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. If the electrode response is slow or drifting, drain and refill the electrode with fresh filling solution, Cat. No. 900011. 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. Refer to the **Interferences** section.

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/water.

Warranty

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

Ordering Information

Electrodes

Refer to the **Introduction** section for a complete list of refillable Ag/AgCl pH electrodes.

Accessories

Cat. No.	Description
900011	Ag/AgCl filling solution, 5 x 60 mL bottles
910001	pH electrode storage solution, 475 mL bottle
900020	pH cleaning solution kit, includes 1 x 15 mL bottle each of cleaning solutions A, B, C and D; pipette and beaker
900021	pH cleaning solution A, includes 4 x 15 mL bottles, pipette and beaker
900022	pH cleaning solution B, includes 4 x 15 mL bottles, pipette and beaker
900023	pH cleaning solution C, includes 4 x 15 mL bottles, pipette and beaker
900024	pH cleaning solution D, includes 4 x 15 mL bottles, 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 pH 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 buffers and buffer sizes.

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