



Cat. No. 51910-88

# PLATINUM SERIES pH ELECTRODE



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# Specifications

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Specifications are subject to change without notice.

## Electrode Type

pH combination with temperature probe

## Range

0-14 pH units

## Isopotential Point

7.00  $\pm$ 0.5 pH units (0  $\pm$ 29 mV)

## Electrode Resistance

less than 100 Mohms at 25 °C (new)

## Slope

-58  $\pm$ 3 mV at 25 °C

## Temperature Range

Routine Use – 0 to 45 °C (32 to 113 °F)

Occasional Use – 0 to 100 °C (32 to 212 °F)

## Storage

-40 to 50 °C (-40 to 122 °F)

## Reference Half Cell

Ag/AgCl/2.2 M KCl in 40% glycerol gel

## Dimensions

Tip Diameter–12.3 mm (0.485 inches)

Tip Length–116 mm (4.55 inches)

Total Length–241 mm (9.5 inches)

Cable Length–0.91 m (36 inches)

## Cable Connector

- *sension* 5-Pin Connector (Cat. No. 51910-00)
- Hach One™ Meter Series BNC & 3.5 mm Phone Connector (Cat. No. 51910-11)
- EC Series BNC & DIN Connector (Cat. No. 51910-22)

## Fill Solution

KCl Cartridges, Reference Gel (Cat. No. 25469-00)



# Safety Precautions

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Please read this entire manual before unpacking, setting up, or operating this instrument. Pay particular attention to all danger and caution statements. Failure to do so could result in serious injury to the operator or damage to the equipment.

To ensure the protection provided by this equipment is not impaired, do not use or install this equipment in any manner other than that which is specified in this manual.

## Use of Hazard Information

If multiple hazards exist, this manual will use the signal word (Danger, Caution, Note) corresponding to the greatest hazard.

### ***DANGER***

*Indicates a potentially or imminently hazardous situation which, if not avoided, could result in death or serious injury.*

### ***CAUTION***

*Indicates a potentially hazardous situation that may result in minor or moderate injury.*

### ***NOTE***

*Information that requires special emphasis.*

## Precautionary Labels

Read all labels and tags attached to the instrument. Personal injury or damage to the instrument could occur if not observed.



This symbol, if noted on the instrument, references the instruction manual for operational and/or safety information.





# Section 1 Introduction

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## 1.1 Electrode Description

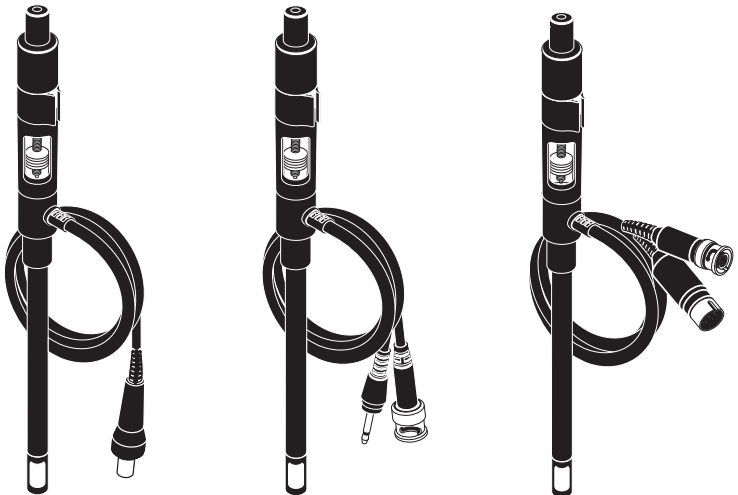
The *sensio*<sup>™</sup> Platinum Series pH Electrode (*Figure 1*) with a renewable, free flowing reference junction is a reliable electrode specifically designed for fast, accurate pH measurement.

Figure 1 *sensio*<sup>™</sup> Platinum Series pH Electrodes

Platinum Series pH Electrode with Temperature Probe (for use with *sensio* pH meters) **(Cat. No. 51910-00)**

Platinum Series pH Electrode with Temperature Probe, BNC, & 3.5 mm Connector (for use with Hach One<sup>™</sup> Series pH meters) **(Cat. No. 51910-11)**

Platinum Series pH Electrode with Temperature Probe, BNC & DIN Connector (for use with EC series pH meters) **(Cat. No. 51910-22)**



The Platinum Series pH Electrode uses a silver/silver chloride reference element with a free-flowing junction. When the dispenser button is pressed, electrolyte gel is dispensed past the reference element to the reference junction.

The Platinum Series pH Electrode, Model 51910, uses a full range pH glass that balances speed of response, full range, and longevity. It is suitable for a wide variety of samples, including hard-to-measure, pure water samples. If using the *sens<sup>i</sup>on* System, the meter will automatically account for buffer temperatures during calibration. The Auto Buffer Recognition/Auto Temperature Compensation calibration program built into *sens<sup>i</sup>on* meters contains accurate pH profiles for buffers of pH 4.01, 6.86, 7.00, and 10.0 at temperatures from 0 to 60 °C.

## 1.2 Electrolyte Description

In a conventional electrode, a frit restricts the release of electrolyte into the sample. In the Platinum Series electrodes, the medium viscosity electrolyte gel acts as a restriction device. Fresh reference electrolyte is supplied from a replaceable cartridge inside the electrode body by depressing the dispenser button. By refreshing the electrolyte at the reference junction, the Hach's free-flowing reference system eliminates junction potential errors caused by clogged frits. The gelling agent is non-ionic and does not interfere with the free flow of ions across the reference junction. Proper use and care of the reference half cell extends its life.

## 1.3 Preparing the Electrode for Use

### 1.3.1 Assembling the Electrode

New electrodes are shipped with a soaker bottle to keep the glass bulb hydrated. Remove the electrode from the soaker bottle and prepare the electrode as follows:

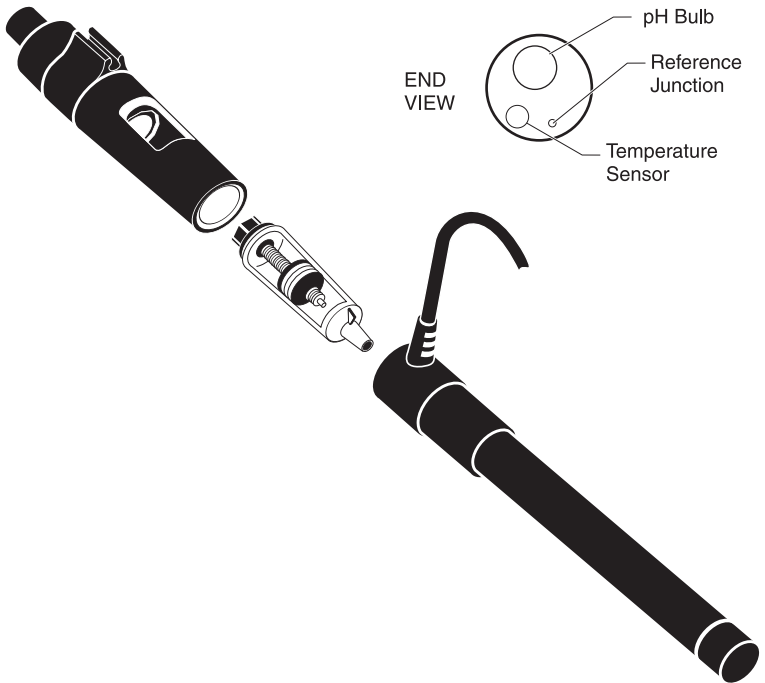
1. Remove the cap from the electrolyte cartridge. Align the fins on the cartridge with the grooves on the electrode body. Press the cartridge firmly into the inlet tube of the

electrode body and rotate the cartridge clockwise until it is seated (*Figure 2*).

- Place the dispenser unit over the electrolyte cartridge. Screw the dispenser unit onto the electrode body until it stops turning. **Do not over tighten.**

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Figure 2 Assembling the Platinum Series Electrode



**Note:** *The electrode will be automatically primed by screwing the dispenser unit onto the electrode body.*

- If electrolyte gel is not visible at the reference outlet, depress the pump button until it clicks; release the button. Repeat this procedure until gel is visible at the reference outlet. Alternatively, fully depress the button and rotate it clockwise until gel is visible at the reference outlet (1 to 3 rotations).

4. Rinse the electrode with deionized water and blot dry with a paper towel. **Do not scrub the bulb.**
5. To remove an empty cartridge, unscrew the dispenser unit and rotate the cartridge counterclockwise while gently pulling it out of the electrode.

### 1.3.2 Conditioning the Electrode

When a pH bulb is immersed in an aqueous solution, a hydrated layer slowly forms at the glass/liquid interface. The formation characteristics of this layer depend upon the type of glass, the age of the glass, the previous usage history of the glass, the temperature and ionic strength of the aqueous solution, etc. This hydrated layer affects the sensing properties of the bulb (charge transfer, and ion transport). A dry bulb will simply not function.

To ensure the full development of the hydrated layer, electrodes should be conditioned for several minutes in a solution comparable to the sample in terms of pH and ionic strength. Some samples may require special conditioning. See specific applications for details.

#### 1.3.2.1 Normal Conditioning

**(For routine measurements in samples of moderate to high conductivity, approximately 150  $\mu\text{S}$  and greater):**

**Initial use:** During shipping, the electrode is kept hydrated by a soaker bottle containing electrode solution. Remove the bottle by loosening the cap. Save the bottle for reuse.

**Between uses:** Between sample measurements of medium to high conductivity, store the electrode in Hach electrode storage solution, a pH 6.35/1.7 M KCl buffer solution. The solution keeps the bulb hydrated and prevents the reference gel from solidifying in the reference junction. Hach electrode storage solution is available in powder pillow form for dilution with deionized water or as a prepared solution. The reusable soaker bottle is convenient for field or laboratory use.

### 1.3.2.2 Low Ionic Strength (LIS) Conditioning (For measurements in samples of low ionic strength, approximately 150 $\mu\text{S}/\text{cm}$ or less):

**Initial use:** Before measuring a LIS sample, pre-soak the electrode in a solution similar to the sample in ionic strength and pH for 10 to 15 minutes. Remove the electrode from this solution and click the reference electrolyte dispenser until gel emerges from the tip. Rinse the electrode with deionized water from a wash bottle. Blot excess liquid with a soft paper towel. Place the electrode in the sample.

**Between uses:** Between uses, in intervals of up to a few hours, the electrode can be stored in the sample (if not an extreme pH), or in a neutral LIS solution such as tap water. Before measuring a new sample, refresh the reference electrolyte gel by clicking the dispenser until fresh gel emerges and carefully rinse the electrode to prevent sample contamination.

## 1.4 Measuring Hints

These suggestions will improve the accuracy of your calibration and sample measurement.

- Dispense electrolyte if reading becomes unstable, erratic, or if stabilization takes too long. An unstable reading may also indicate an air bubble in the reference line. Remove the electrode from the sample and invert it to view the reference junction. Depress the dispenser button repeatedly until the bubble is expelled (5 to 10 clicks should be sufficient). Rinse with sample and blot to dry. Immerse the electrode in the sample.
- Allow the potential to stabilize completely (<1 mV/minute drift) before accepting a calibration point or sample reading. Meters set to higher resolutions will take longer to stabilize than meters set to lower resolutions.
- Use calibration standards and samples that are at the same temperature to improve accuracy.
- Use fresh calibration standards to achieve greater accuracy.

- Thoroughly rinse and blot the electrode dry between sample measurements. Remove the bulb guard before measuring low ionic strength samples to prevent transferring contaminants to the next sample, or rinse with small volumes of sample.
- Analyze samples shortly after collecting them. Weakly buffered alkaline solutions can absorb carbon dioxide causing downward drift of pH readings. Cover samples if necessary. When measuring LIS samples requiring high levels of accuracy, use the LIS accessory sample chamber.
- A multi-point calibration will ensure more accurate measurements than a single point calibration.

### 1.5 Checking the Slope

After calibrating the electrode with fresh buffer, check the slope using the *sension* meter's calibration review option. A slope of  $-58 \pm 3$  mV indicates a properly functioning electrode.

### 1.6 Accessories

#### 1.6.1 Hach Low Ionic Strength Sample Chamber Kits

The Hach Low Ionic Strength Sample Chamber Kit (Cat. No. 51899-00) prevents sample contamination by carbon dioxide. When a sample absorbs carbon dioxide from the atmosphere, carbonic acid forms and the pH of the sample decreases.

The kit includes a sample chamber with a cap suitable for:

- Measuring the pH of a grab sample while reducing the sample's exposure to the atmosphere.
- Measuring the pH of a flow or plug-flow sample with no exposure to the atmosphere.

### 1.6.2 Sample Bottles

Sample bottles designed for use with or without the Low Ionic Strength Sample Chamber are available in two grades of cleanliness:

- General purpose bottles suitable for most drinking water and wastewater tests.
- Bottles cleaned and certified according to EPA specifications that are suitable for EPA reporting and for testing ultrapure water.

### 1.7 General Applications

*SECTION 2* describes specific applications for the Platinum Series pH Electrode. General applications include:

- Monitoring the pH of low ionic strength liquids such as boiler, feedwater, and condensate.
- Environmental and ecological studies of natural waters such as lakes, rivers, precipitation, and streams.
- Water and wastewater treatment to monitor influent and effluent quality.
- Agricultural applications including soil, fertilizer, food, and feed.
- Chemical and biological research.
- Industrial processes in the manufacture of foods, beverages, pharmaceuticals, dyes, photographic film, plating, and chemicals.
- Continuous sampling in aqueous samples up to 45 °C and intermittent sampling in aqueous samples up to 100 °C.

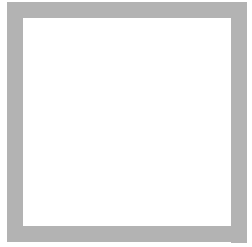
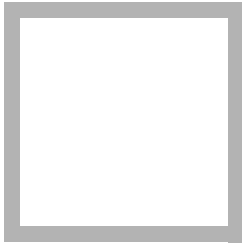
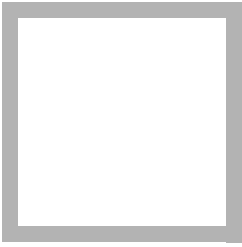
For information regarding applications not described in this manual, contact Hach Technical and Customer Service.





## Section 2 Applications

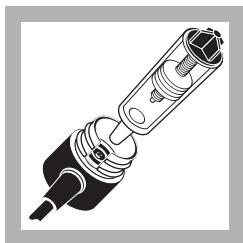
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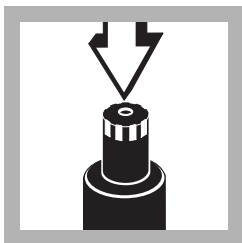
## pH, Water and Wastewater (above 150 $\mu\text{S}/\text{cm}$ )

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1. Install the Potassium Chloride Electrolyte Gel Cartridge in the Platinum Series pH Electrode. (See *Section 1.3.1* on page 10 for assembly instructions.)

**Note:** This procedure contains instructions for the *sens<sup>ion</sup>™2*. However, any Hach *sens<sup>ion</sup>* meter may be used for this analysis.

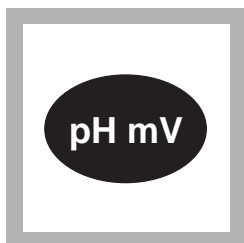


2. Prime the electrode by pushing the dispenser button until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet.



3. Connect the electrode to the *sens<sup>ion</sup>2* pH/ISE meter.

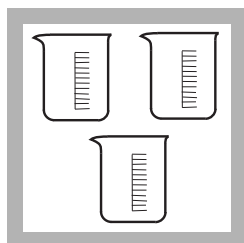
**Note:** Ensure that the electrode has been conditioned according to instructions in *Section 1.3.2* on page 12.



4. Turn on the meter by pressing **I/O**. Press **PH MV** until the display shows **pH**.



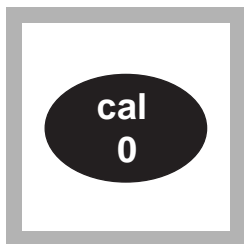
5. Press **SETUP**. Press the up arrow three times. Press **ENTER** to toggle to the number of desired decimal places, then **EXIT** to leave setup.



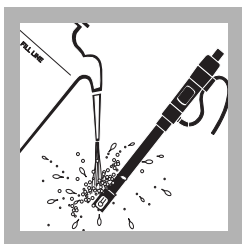
6. In three 50-mL beakers or cups, prepare buffers of 4.0, 7.0, and 10.0 pH.

*Note: The sample pH should fall within the range of the calibration buffers.*

*Note: pH 6.86 buffer may be used instead of pH 7.0. Autobuffer recognition for either pH 6.86 or 7.0 is user selectable in the **sensio**n meter setup.*



7. Press **CAL**. The display will show: **Standard 1?**



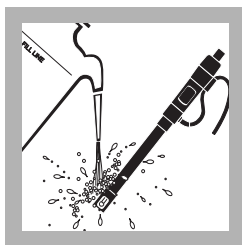
8. Rinse electrode in deionized water and blot dry.



9. Place the electrode in pH 7.0 buffer. Press **ENTER**. The display shows:

**Stabilizing...**

***Note:** Temperature variation causes changes in buffer pH. Hach **sens**ion meters correct for these changes during calibration when using buffers of pH 4, 6.86, 7, and 10.*

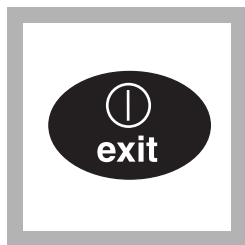


10. When a stable pH is determined, the display will show **Standard 2?**. Remove the electrode from the cup. Rinse with deionized water and blot dry.

*Note: The meter will select a stable reading using default meter parameters and the specified resolution. To override the default meter parameters, see the meter manual.*

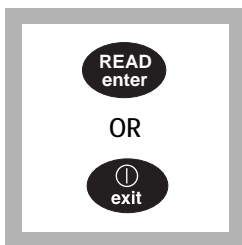


11. Place the electrode in the 4.0 (or 10.0) pH buffer. Press **ENTER**.

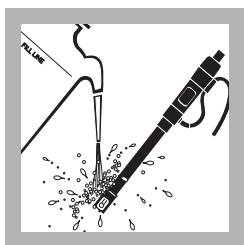


12. After the last calibration point has stabilized and the display reads **Standard 3?**, press **EXIT**.

For a three-point calibration, repeat steps 10-11 with an additional buffer.



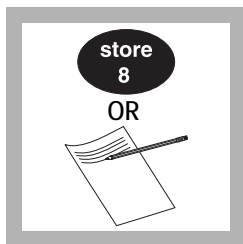
13. The display will show **Store?**. Press **ENTER** to store the calibration or **EXIT** to leave the calibration mode without storing the values.



14. Remove electrode from buffer. Rinse with deionized water followed by a small amount of sample and blot dry.



15. Place the electrode in the sample.



16. Store or record the pH and temperature readings when they stabilize.

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### Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Analyze samples immediately, preferably in the field.

### Accuracy Check

#### Checking Electrode Response

An electrode is responding properly if its calibration slope is  $-58 \pm 3$  mV per pH unit.

#### Checking Calibration Accuracy

Returning the electrode to a calibration buffer and determining the pH provides a good test of the system. Rinse and recondition the electrode before measuring subsequent samples.

#### Checking the Precision of the Sample Reading

When practical, measure the pH of the sample several times and report the average pH. *sension2* meters will store and calculate the average of up to 99 readings.

### Method Performance

#### Precision

In a single lab using an ASTM Substitute Wastewater Standard, specification number D5905-96, and two electrodes with a single *sensIon2*, a single operator obtained a standard deviation of 0.004 pH. Each electrode was exposed to seven test solutions with no rinsing in between and with a default stability of 0.5 mV/min.

### Interferences

Sodium error may occur in samples with pH 10 or higher. See *Section 4.2* on page 48.

### Summary of Method

Water with relatively high conductivity typically has a fairly high buffer capacity. Slight pH changes due to absorption of carbon dioxide are usually not significant. If the sample conductivity is not known and high accuracy is desired, follow either the LIS or high purity methods.

The Platinum Series Combination pH Electrode responds to the hydrogen ion concentration (activity) by developing an electrical potential. At a constant temperature, this potential varies linearly with the pH of the solution being measured. The electrode has a free-diffusion junction that eliminates clogging problems and has been proven to provide fast, accurate results.



**REQUIRED REAGENTS AND APPARATUS**

Description	Quantity Required		Unit	Cat. No.
	Per Test			
Platinum Series Combination pH Electrode				
w/Temp.....	1		each....	51910-00
<i>sensio</i> <sup>TM</sup> 2 Portable pH/ISE Meter....	1		each....	51725-10
Potassium Chloride Electrolyte Cartridge	1	2/pkg...		25469-02

**OPTIONAL REAGENTS**

Buffer, Powder Pillow

pH 4.01, color-coded red.....	15/pkg.....	22269-95
pH 6.86 .....	15/pkg.....	14098-95
pH 7.00, color-coded yellow.....	15/pkg.....	22270-95
pH 10.00, color-coded blue.....	15/pkg.....	22271-95
Buffer Solution, pH 4 (red).....	500 mL.....	22834-49
Buffer Solution, pH 7 (yellow).....	500 mL.....	22835-49
Buffer Solution, pH 10 (blue).....	500 mL.....	22836-49
Singlets, pH 4.01/7.00.....	10/pkg.....	27699-20
Singlets, pH 7.00/10.01.....	10/pkg.....	27698-20
Singlets, Electrode Rinse Solution .....	20/pkg.....	27703-20
Storage Solution, pH Electrode .....	500 mL.....	27565-49
Water, deionized.....	4 L.....	272-56

**OPTIONAL APPARATUS**

Sample Bottles

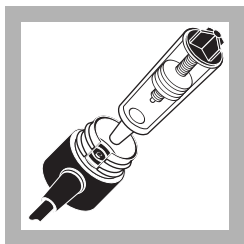
General Purpose with Screw-cap,

polypropylene, 500-mL.....	each.....	27581-01
Cleaned and certified, HDPE,		
suitable for EPA reporting, 500-mL .....	each.....	27582-01
<i>sensio</i> <sup>TM</sup> 1 Portable pH Meter.....	each.....	51700-10
<i>sensio</i> <sup>TM</sup> 3 Laboratory pH Meter .....	each.....	51750-10
<i>sensio</i> <sup>TM</sup> 4 Laboratory pH/ISE Meter .....	each.....	51775-10



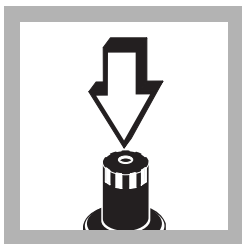
# pH, High Purity Water ( $\approx 2$ to $50 \mu\text{S}/\text{cm}$ )

For boiler, natural, and deionized water

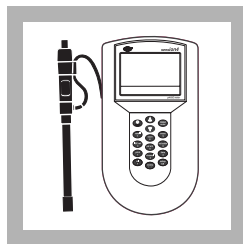


1. Install the Potassium Chloride Electrolyte Gel Cartridge in the Platinum Series pH Electrode. (See *Section 1.3.1* on page 10 for assembly instructions.)

**Note:** The Hach *sens<sup>ion</sup>™4* meter is used for this analysis.



2. Prime the electrode by pushing the dispenser button until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet.



3. Connect the electrode to the *sens<sup>ion</sup>4* pH/ISE meter.

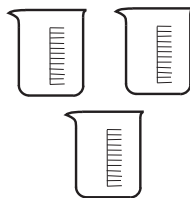
**Note:** Ensure that the electrode has been conditioned according to instructions in *Section 1.3.2* on page 11.



pH mV



setup



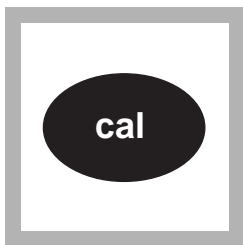
4. Turn on the meter by pressing **I/O**. Press **PH MV** until the display shows **pH**.

5. Press **SETUP**. Press the up arrow three times. Press **ENTER** to toggle to the number of desired decimal places, then **EXIT** to leave setup.

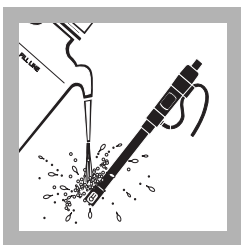
6. In three 50-mL beakers or cups, prepare buffers of 4.0, 7.0, and 10.0 pH.

*Note: The sample pH should fall within the range of the calibration buffers.*

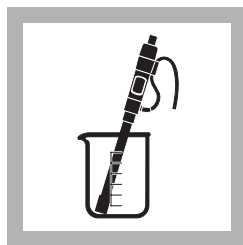
*Note: pH 6.86 buffer may be used instead of pH 7.0. Autobuffer recognition for either pH 6.86 or 7.0 is user selectable in the **sens<sup>ion</sup>** meter setup function.*



7. Press **CAL**. The display will show: **Standard 1?**



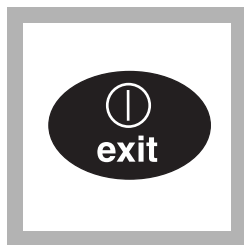
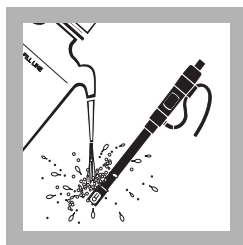
8. Rinse electrode in deionized water and blot dry.



9. Place the electrode in pH 7.0 buffer. Press **ENTER**. The display shows:

**Stabilizing...**

***Note:** Temperature variation causes changes in buffer pH. Hach sens*ion* meters correct for these changes during calibration when using buffers of pH 4, 6.86, 7, and 10.*



10. When a stable pH is determined, the display will show **Standard 2?**.

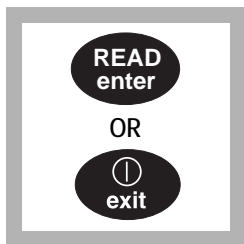
Remove the electrode from the cup, rinse, and blot dry.

**Note:** The meter will select a stable reading using default meter parameters and the specified resolution. To override the default meter parameters, see the *sensio<sup>n</sup>4* meter manual.

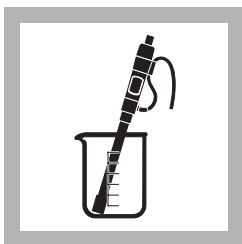
11. Place the electrode in 4.0 (or 10.0) pH buffer. Press **ENTER**.

12. After the last calibration point has stabilized and the display reads **Standard 3?**, press **EXIT**.

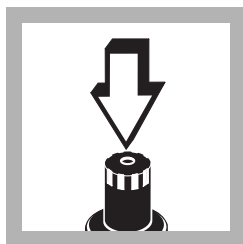
**Note:** For a three-point calibration, repeat steps 10-11 with an additional buffer.



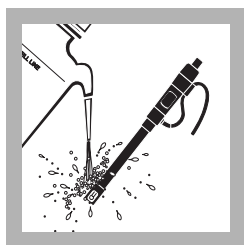
13. The display will show **Store?**. Press **ENTER** to store the calibration or **EXIT** to leave the calibration mode without storing the values.



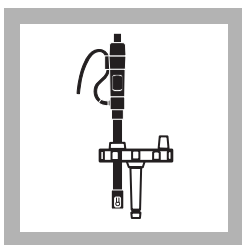
14. Condition the electrode for 10 minutes in deionized water.



15. Remove from deionized water. Prime the reference junction by clicking the pump until fresh gel emerges.

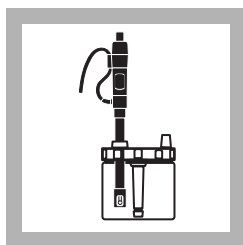


16. Rinse the electrode with deionized water or sample and blot dry.



17. Place the electrode into the clean LIS Sample Chamber Lid.

**Note:** Make sure that the electrode will be completely submerged in the sample.

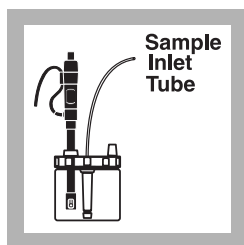


18. Screw the cap and attached electrode onto a clean sample bottle.

**Note:** EPA certified clean bottles are available. See **OPTIONAL APPARATUS** on page 34.

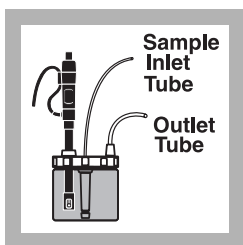
## pH, High Purity Water, continued

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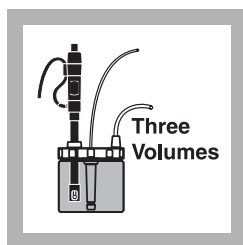


19. Connect the inlet tube from the sample source to the sample chamber.

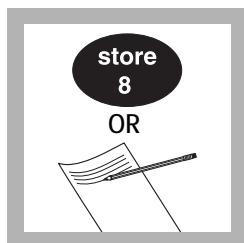
*Note: The inlet tube extends directly to the bottom of the sample chamber.*



20. Adjust inlet flow to slowly fill the chamber from the bottom up. Allow excess sample to flow from the overflow tube.



21. Allow three volumes to pass through the chamber. Shut off sample flow.



22. Store or record the pH and temperature readings after they stabilize.

---

## Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Analyze samples immediately, preferably in the field.



## Accuracy Check

### Checking Electrode Response

An electrode is responding properly if its calibration slope is  $-58\pm 3$  mV per pH unit.

### Checking Calibration Accuracy

Returning the electrode to a calibration buffer and determining the pH provides a good test of the system. Rinse and recondition the electrode before measuring subsequent samples.

### Checking the Precision of the Sample Reading

When practical, measure the pH of the sample several times and report the average pH. *sensioN4* meters will store and calculate the average of up to 99 readings.

## Method Performance

### Precision

In a single lab using a  $1.8 \mu\text{S}/\text{cm}$  standard solution of pH 7.0 and two electrodes with a single *sensioN<sup>TM</sup>2*, a single operator obtained a standard deviation of 0.05 pH. Each electrode was exposed to seven test solutions with no rinsing in between and with a default stability of 0.5 mV/min.

## Interferences

Carbon dioxide absorption from the atmosphere and contamination from improperly cleaned sample containers interferes with accurate pH measurements.

## Summary of Method

High purity water has little buffering capacity. As a result, small amounts of impurities can cause large changes in pH. This method minimizes atmospheric (mainly carbon dioxide) contamination of the sample.

The Platinum Series Combination pH Electrode responds to the hydrogen ion concentration (activity) by developing an electrical potential. At a constant temperature, this potential varies linearly with the pH of the solution being measured. The

## pH, High Purity Water, continued

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electrode has a free-diffusion junction that eliminates clogging problems and provides fast, accurate results.

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### REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Platinum Series™ Combination pH Electrode w/Temp.....	1	each	51910-00
<i>sensION</i> ™ 4 Laboratory pH/ISE Meter, 115 VAC.....	1	each	51775-10
<i>sensION</i> ™ 4 Laboratory pH/ISE Meter, 230VAC .....	1	each	51775-11
Potassium Chloride Electrolyte Cartridge.....	1	2/pkg	25469-02
Hach Low Ionic Strength Sample Chamber Kit.....	1	each	51899-00

### OPTIONAL REAGENTS

Buffer, Powder Pillow pH 4.01, color-coded red.....	15/pkg	.....	22269-95
pH 6.86 .....	15/pkg	.....	14098-95
pH 7.00, color-coded yellow.....	15/pkg	.....	22270-95
pH 10.00, color-coded blue.....	15/pkg	.....	22271-95
Buffer Solution, pH 4 (red) .....	500 mL	.....	22834-49
Buffer Solution, pH 7 (yellow) .....	500 mL	.....	22835-49
Buffer Solution, pH 10 (blue).....	500 mL	.....	22836-49
Singlets, pH 4.01/7.00 .....	10/pkg	.....	27699-20
Singlets, pH 7.00/10.01.....	10/pkg	.....	27698-20
Singlets, Electrode Rinse Solution .....	20/pkg	.....	27703-20
Storage Solution, pH Electrode .....	500 mL	.....	27565-49
Water, deionized.....	4 L	.....	272-56

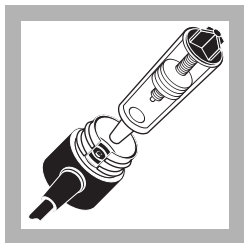
### OPTIONAL APPARATUS

Sample Bottles General Purpose with Screw-cap, polypropylene, 500 mL .....	each	.....	27581-01
Cleaned and certified, HDPE, suitable for EPA reporting, 500 mL.....	each	.....	27582-01

# pH, Low Ionic Strength (LIS) Water

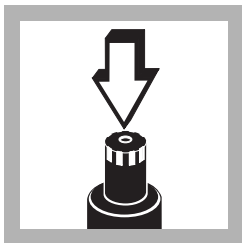
(50 to 150  $\mu\text{S}/\text{cm}$ )

For drinking water and natural waters



1. Install the Potassium Chloride Electrolyte Gel Cartridge in the Platinum Series pH Electrode. (See *Section 1.3.1* on page 10 for assembly instructions.)

**Note:** The Hach *sens<sup>ion</sup>™2* meter is used for this analysis.



2. Prime the electrode by pushing the dispenser button until gel comes out of the reference junction. Rinse excess gel from the tip and the outlet.



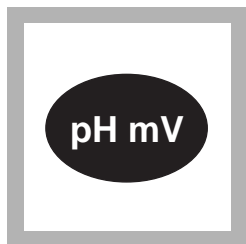
3. Connect the electrode to the *sens<sup>ion</sup>2* pH/ISE meter.

**Note:** Ensure that the electrode has been conditioned according to instructions in *Section 1.3.2* on page 12.

**Note:** Ensure meter is set up for 5-pin connector.

## pH, Low Ionic Strength (LIS) Water, continued

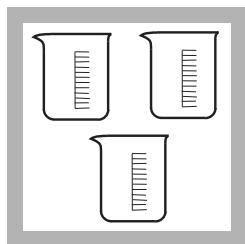
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4. Turn on the meter by pressing **I/O**. Press **PH MV** until the display shows **pH**.



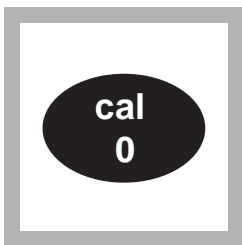
5. Press **SETUP**. Press the up arrow three times. Press **ENTER** to toggle to the number of desired decimal places, then **EXIT** to leave setup.



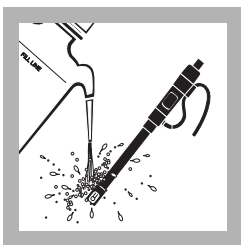
6. In three 50-mL beakers or cups, prepare buffers of 4.0, 7.0, and 10.0 pH.

*Note: The sample pH should fall within the range of the calibration buffers.*

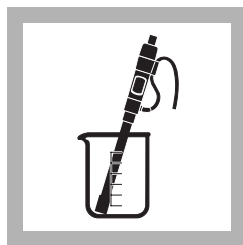
*Note: pH 6.86 buffer may be used instead of pH 7.0. Autobuffer recognition for either pH 6.86 or 7.0 is user selectable in the **sension** meter setup function.*



7. Press **CAL**. The display will show: **Standard 1?**



8. Rinse electrode in deionized water and blot dry.



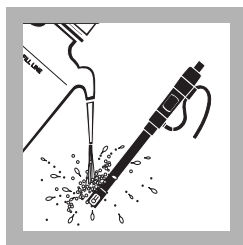
9. Place the electrode in pH 7.00 buffer. Press **ENTER**. The display shows:

**Stabilizing...**

***Note:** Temperature variation causes changes in buffer pH. Hach **sens**ion meters correct for these changes during calibration when using buffers of pH 4, 6.86, 7, and 10.*

## pH, Low Ionic Strength (LIS) Water, continued

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10. When a stable pH is determined, the display will show **Standard 2?**.

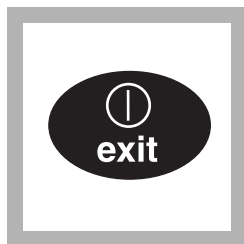
Remove the electrode from the cup. Rinse with deionized water and blot dry.

**Note:**

The *sension™4* meter will select a stable reading using default meter parameters and the specified resolution. To override the default meter parameters, see the meter manual.



11. Place the electrode in the 4.0 (or 10.0) pH buffer. Press **ENTER**.

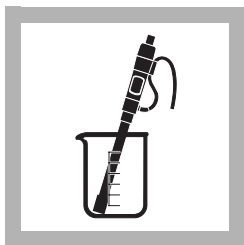


12. After the last calibration point has stabilized and the display reads **Standard 3?**, press **EXIT**.

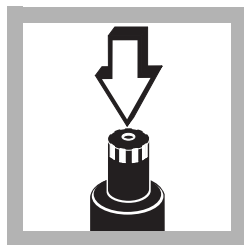
**Note:** For a three-point calibration, repeat steps 10-11 with an additional buffer.



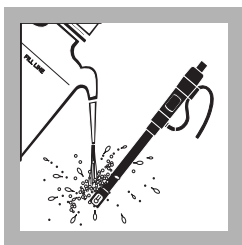
13. The display will show **Store?**. Press **ENTER** to store the calibration or **EXIT** to leave the calibration mode without storing the values.



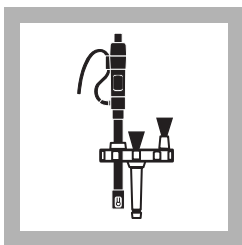
14. Condition the electrode in deionized water for 10 minutes.



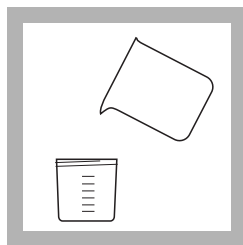
15. Remove the electrode from the deionized water and prime the electrode by clicking the pump until fresh gel emerges.



**16.** Rinse electrode with a small volume of deionized water or sample and blot dry.

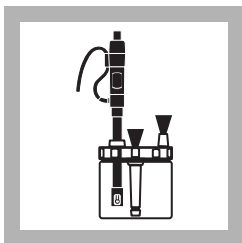


**17.** Fit the electrode into the clean LIS sample chamber lid and plug inlet and outlet ports with stoppers.

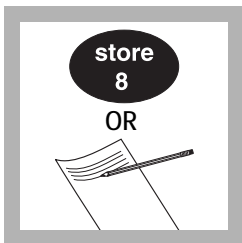


**18.** If not using a sample collection bottle that fits the sample chamber, transfer the sample to the LIS sample chamber bottle.

Completely fill the sample chamber, leaving as little air space as possible in the chamber.



**19.** Screw the cap and attached electrode onto the sample bottle.



**20.** Store or record the pH and temperature readings when they stabilize.

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## Sampling and Storage

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Analyze samples immediately, preferably in the field.

### Accuracy Check

#### Checking Electrode Response

An electrode is responding properly if its calibration slope is  $-58 \pm 3$  mV per pH unit.

#### Checking Calibration Accuracy

Returning the electrode to a calibration buffer and determining the pH provides a good test of the system. Rinse and recondition the electrode before measuring subsequent samples.

#### Checking the Precision of the Sample Reading

When practical, measure the pH of the sample several times and report the average pH. *sensION2* meters will store and calculate the average of up to 99 readings.

### Method Performance

#### Precision

In a single lab using a  $150 \mu\text{S}/\text{cm}$  standard solution of pH 7.1 and two electrodes with a single *sensION2*, a single operator obtained a standard deviation of 0.006 pH. Each electrode was exposed to seven test solutions with no rinsing in between and with a default stability of 0.5 mV/min.

### Interferences

Carbon dioxide absorption from the atmosphere and contamination from improperly cleaned sample containers interferes with accurate pH measurements.

### Summary of Method

LIS solutions have a small buffering capacity and are only slightly resistant to pH changes. This method reduces atmospheric (mainly carbon dioxide) contamination to the sample.

The Platinum Series Combination pH Electrode responds to the hydrogen ion concentration (activity) by developing an electrical potential. At a constant temperature, this potential varies linearly with the pH of the solution being measured. The



## pH, Low Ionic Strength (LIS) Water, continued

electrode has a free-diffusion junction that eliminates clogging problems and has been proven to provide fast, accurate results.

### REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Platinum Series Combination pH Electrode			
w/Temp.....	1	each....	51910-00
<i>sensION</i> <sup>TM</sup> 2 Portable pH/ISE Meter....	1	each....	51725-10
Potassium Chloride Electrolyte Cartridge	1.....	2/pkg..	25469-02
Hach Low Ionic Strength Sample Chamber	1	each...	51899-00

### OPTIONAL REAGENTS

#### Buffer, Powder Pillow

pH 4.01, color-coded red.....	15/pkg.....	22269-95
pH 6.86.....	15/pkg.....	14098-95
pH 7.00, color-coded yellow.....	15/pkg.....	22270-95
pH 10.00, color-coded blue.....	15/pkg.....	22271-95
Buffer Solution, pH 4 (red).....	500 mL.....	22834-49
Buffer Solution, pH 7 (yellow).....	500 mL.....	22835-49
Buffer Solution, pH 10 (blue).....	500 mL.....	22836-49
Singlets, pH 4.01/7.00.....	10/pkg.....	27699-20
Singlets, pH 7.00/10.01.....	10/pkg.....	27698-20
Singlets, Electrode Rinse Solution.....	20/pkg.....	27703-20
Storage Solution, pH Electrode.....	500 mL.....	27565-49
Water, deionized.....	4 L.....	272-56

### OPTIONAL APPARATUS

#### Sample Bottles

##### General Purpose with Screw-cap,

polypropylene, 500-mL..... each.....27581-01

##### Cleaned and certified, HDPE,

for EPA reporting, 500-mL..... each..... 27582-01

##### *sensION*<sup>TM</sup> 1 Portable pH Meter

with electrode..... each.....51700-10

##### *sensION*<sup>TM</sup> 3 Laboratory pH Meter

with electrode..... each.....51750-10

##### *sensION*<sup>TM</sup> 4 Portable pH/ISE Meter

with electrode..... each.....51775-10



## Section 3    Electrode Maintenance

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The Platinum Series pH electrode contains a sensing glass bulb and a liquid reference junction optimized for performance in difficult, cold, neutral, and low ionic strength (LIS) solutions. This sensitive instrument has been designed to give trouble-free use, but requires careful handling to extend longevity. This section explains methods for conditioning, cleaning, and storing the Platinum Series pH electrode.

### 3.1 Storing the Electrode

Proper electrode storage requires different approaches based on how long the electrode will be stored, how quickly the electrode needs to be used, and the type of sample being measured. Storage affects the reference electrolyte gel, the Ag/AgCl reference element, and the pH sensing glass bulb.

**Intermittent storage:** Between uses, store the electrode in solutions of similar ionic strength and pH to the samples of interest. Before measuring a new sample, refresh the reference electrolyte gel by clicking the dispenser until fresh gel emerges. Carefully rinse the electrode to prevent sample contamination.

**Overnight storage:** Store the electrode in Hach pH electrode storage solution to keep the electrode hydrated. The KCl will not leach excessively from the electrolyte gel overnight. Prior to use, click the electrolyte gel dispenser. A dilute gel/storage solution will initially be ejected from the reference junction tube. The reference gel of thicker viscosity will follow. Eliminating the dilute gel/storage solution will guarantee continuity of the reference junction with the sample. Blot the reference junction with a tissue to clearly see that the electrolyte gel, not gel diluted with storage solution, is emerging.

**Longer-term storage:** To store electrodes for longer periods, soak the electrode in storage solution (*Overnight storage*, above) and re-establish gel at the reference junction on a daily basis to keep the electrode ready for use. If the electrode soaks for longer periods without purging the diluted electrolyte, the

entire reference electrolyte gel cartridge can become diluted through diffusion. Typically this will not harm the Ag/AgCl reference element, but the electrolyte cartridge itself will be ruined. This storage method keeps the electrode ready to use, but requires purging the gel every day.

**Shelf Storage:** For very long-term storage, store the electrode dry. To empty the reference half-cell of electrolyte gel, remove and discard the electrolyte cartridge. Use a syringe with male luer fitting and no needle to inject deionized water through the reference cell to flush out the reference electrolyte gel. Expel the water injected into the reference cell with an air-filled syringe. Replace the electrode storage bottle over the end of the probe and tighten the cap. Refill the bottle as required with electrode storage solution (Cat. No. 27565-49).

### 3.2 Cleaning the Electrode

A contaminated glass bulb or fouled electrode may cause slow response times. Clean the electrode only after conducting the steps described in *Section 5 Troubleshooting* or when the electrode is known to be dirty. Don't clean the bulb more frequently than necessary, or bulb life may shorten. Follow the instructions below to clean the electrode according to the type of contaminant present:

**General contamination**—Immerse the electrode tip in 0.1 N hydrochloric acid followed by immersion in 0.1 N sodium hydroxide and again in 0.1 N hydrochloric acid, each for a 2-minute period. Rinse with deionized water and soak in deionized water for at least 15 minutes.

**Oils and fats**—Immerse the electrode tip in a detergent solution such as Alconox™. Use a soft brush or ultrasonic bath if necessary. **Avoid scratching the glass bulb.**

**Organic films**—Use an appropriate solvent, such as methanol or acetone.

*Note: Keep the cable and connector away from dirt, abrasives, and harsh solvents.*

After cleaning, refresh reference half cells by pumping fresh electrolyte through them. If the electrode has been sitting in a sample for several weeks, the reference gel will become diluted. In this case, discard the cartridge and replace it with a fresh one.

If these steps fail to improve electrode response, complete the *Electrode Service Request Questionnaire* and contact Technical Support.



# Section 4 Platinum Series pH Electrode Characteristics

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## 4.1 Theory of Operation

pH is a measure of the hydrogen ion activity in a solution and is defined as:  $-\log_{10} a_{H^+}$  where  $a_{H^+}$  is the activity of the hydrogen ion. The 0-14 range of pH measurement is the measurement of a difference in hydrogen ion concentration of 100,000,000,000,000 ( $1 \times 10^{14}$ ). This means that at pH 0, the hydrogen ion concentration is  $1 \times 10^{14}$  times greater than at pH 14. This also means that the hydroxyl ion concentration at pH 14 is  $1 \times 10^{14}$  times greater than at pH 0.

When the hydrogen and hydroxyl ions are present in equal numbers (the neutral point), the pH is 7. pH values from 0 to 7 are termed acidic and those from 7 to 14 are termed basic. Note that a pH change of one unit (for instance from pH 6 to pH 7) is a factor-of-10 change in hydrogen ion concentration.

The glass membrane of a pH electrode responds to the hydrogen ion activity by developing an electrical potential at the glass/liquid interface. At a constant temperature, this potential varies linearly with the pH of the solution being measured. The change in potential per pH unit is the slope of the electrode. The slope of the electrode increases linearly with temperature.

The potential inside the pH glass bulb is fixed by the filling solution, and the reference electrode potential is constant. For these reasons, any change in the potential of the electrode system at a given temperature will be due to any change in the pH of the solution being measured.

Effects of temperature on pH measurements depend on the reference electrode used, pH of the solution within the pH electrode, and pH of the test solution. At a certain pH, temperature will have no effect on the potential of the electrode system. This is known as the isopotential point. Also, at some pH level, the system will exhibit no potential. This is known as the zero potential point. Both the isopotential point and the zero potential point are features designed into electrodes. Each electrode is designed so the isopotential and zero potential points are at pH 7 to minimize temperature effects at this

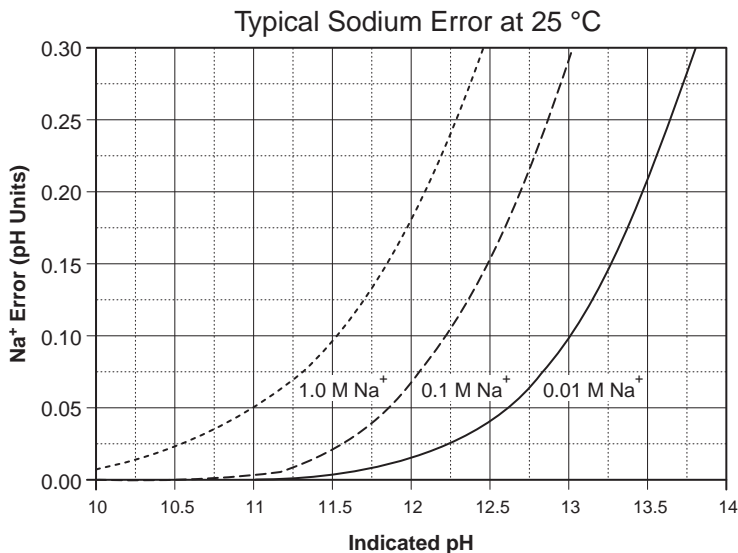
## Section 4, continued

calibration point. At 25 °C, the slope of an electrode performing at 100% efficiency will decrease by 59.2 mV for every unit increase in pH.

### 4.2 Sodium Error Interferences

Sodium error occurs at elevated pH values due to the pH glass' inability to discriminate between sodium ions and acidic H<sup>+</sup> ions (specifically, solvated hydronium ions, H<sub>3</sub>O<sup>+</sup>). This leads to low pH readings. The following graph shows the correlation between sodium concentration, indicated pH reading, and the amount of error associated with the reading at the indicated sodium concentration.

*Note: For indicated readings below pH 11, sodium error is negligible for solutions with a sodium concentration below 0.1 M.*



**Example** — The meter indicates a reading of pH 12.5, and the sodium concentration of the sample is 0.1 M. Locate pH 12.5 on the x-axis. Move vertically to locate the point at which the 0.1 M Na<sup>+</sup> curve crosses the pH 12.5 value. Move horizontally from this point to see the sodium error, 0.15 pH units. Adding this error to the reading will give a corrected sodium pH value of 12.65.



## Section 5 Troubleshooting

Symptom	Cause	Remedy
No response	Electrode is improperly connected to meter.	Check connection.
	If a two-channel meter, is the electrode connected to the displayed channel? (A shorting cap on a channel input will show <b>ZERO</b> on the display.)	Reconnect the electrode to the desired channel or change the displayed channel on the meter.
	Connector is dirty or wet.	<ol style="list-style-type: none"> <li>1. Inspect both male and female connector.</li> <li>2. Clean with mild solvents such as alcohol or acetone.</li> <li>3. Clean and dry with a lint-free cloth or compressed air.</li> </ol>
	Reference junction is blocked.	Press the electrolyte dispenser and see if gel is expelled from the reference junction tube. If the junction is blocked, see <i>Section 1.3.1</i> on page 10.
	pH sensing bulb and reference junction are not in contact with the sample.	Submerge the probe deeper into the sample.
	Cable contains kinks, breaks, loose connectors, etc.	Replace electrode.
	The meter is broken.	<ol style="list-style-type: none"> <li>1. Try another electrode.</li> <li>2. Try the other channel.</li> <li>3. Check and replace batteries, if necessary.</li> <li>4. Put shorting caps on and see if meter "zeros".</li> </ol>
	The meter is not set up to read from the appropriate connector.	In meter setups, select the appropriate connector (5-pin for <i>sensION</i> meters).

## Troubleshooting, continued

Symptom	Cause	Remedy
Out-of-range response	See "No response", above.	The bulb may be broken.
Erratic response	Reference junction contains bubbles.	Push dispenser button and turn clockwise two turns.
	Electrode is not plugged in to selected meter channel.	Plug electrode into meter channel.
	Reference junction has not been properly primed with gel.	Follow instructions in <i>Section 1.3.1</i> on page 10.
	Extreme external electrical fields are present. (The pH cable, though shielded, can act as an antenna.)	Install a shorting cap on the unused meter terminal. Do not use stirrers in LIS solutions. Avoid static electricity, nearby pumps, power supplies, etc.
	pH sensing bulb and reference junction are not in contact with the sample.	Submerge the probe deeper into the sample.
	The sample chemistry is changing.	None.
	The pH of a LIS solution is changing due to CO <sub>2</sub> uptake.	Use LIS Chamber Accessory.
	The bulb is cracked, discolored, or contaminated.	If dirty, clean according to <i>Section 3.2</i> on page 44. If cracked, discard.
The sample container is contaminated.	Use a clean sample container.	

## Troubleshooting, continued

Symptom	Cause	Remedy
Low slope	Bulb is old.	Replace electrode.
	Bulb is dirty.	Clean according to <i>Section 3.2</i> on page 44.
	Standards are inaccurate.	Make sure standards were entered into meter correctly. Use only NIST traceable buffers. Use fresh buffers. Change buffers frequently.
	History of harsh usage.	Replace electrode.
	Cracked bulb.	Replace electrode.
High slope	Buffers are incorrect.	Use appropriate buffers.
	Incorrect measurement or calibration technique.	Follow procedures described in <i>Section 2</i> on page 17.
	Temperature variations in standards.	Keep sample and standards at same temperature.
	Standards contaminated.	Prepare fresh standards.
High offset	Leakage pathway results in stray voltage via internal electrical short.	Return electrode under warranty.
	Reference gel has become diluted or junction is plugged by solidified gel or an air bubble.	Replace cartridge and reprime.
	Cracked bulb.	Replace electrode.
	A 5-pin electrode that is not in use is connected to the 5-pin connector.	Disconnect the 5-pin electrode.
Sluggish response	Sample is cold and of low ionic strength.	Wait patiently. Samples may respond slowly.
	Improper conditioning.	Condition according to <i>Section 1.3.2</i> on page 12.
	Bulb, guard, and electrode stem are dirty.	Clean according to <i>Section 3.2</i> on page 44.



# Electrode Service Request Questionnaire

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1. What model of meter is the electrode being used with?
2. What is the model number of the electrode?
3. What is the complete lot code of the electrode (located on the electrode cable)?
4. What is the date the electrode was purchased?
5. How long has the electrode been in use?
6. What types of samples are being tested?
7. What is the temperature of the samples being tested?
8. How often is the electrode being used?
9. How is the electrode being stored between uses?
10. What is the electrode slope during a typical calibration?
11. If a new electrode, has it been conditioned according to instructions?
12. If the electrode has been in use for a while, what maintenance has been performed?
13. Describe the suspected problem or failure of the electrode.
14. When calling for telephone support, have your meter, electrode, and buffers/standards, along with this completed questionnaire, near the phone before calling.
15. Did you use ISA in samples or standards?
16. Did you use the low range method for LIS and high purity drinking water samples with conductivity below  $150 \mu\text{S}/\text{cm}$ ?
17. Is the sample above pH 12 with a high  $\text{Na}^+$  concentration?



# Glossary

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**Acid**—a chemical compound that contributes hydrogen ions ( $H^+$ ) to an aqueous solution or causes the pH to be less than 7.0.

**Acidic**—A solution or system with a pH less than 7.0.

**Activity**—The measure of work performed by an ion as it moves through a system. The activity is dependent upon the concentration of all ions in the system and the charge associated with the ion.

**Alkali**—A solution or system with a pH greater than 7.0.

**Alkalinity**—Capacity of water to accept hydrogen ions ( $H^+$ ). Indicates presence of carbonate ( $CO_3^{2-}$ ), bicarbonate ( $HCO_3^-$ ), and hydroxyl ( $OH^-$ ) ions.

**Anion**—A negatively charged ion (i.e.,  $NO_3^-$ ,  $Cl^-$ ).

**Base**—A chemical compound that contributes hydroxide ions ( $OH^-$ ) to an aqueous solution or causes the pH to be greater than 7.0.

**Buffer**—

1. A compound, mixture of compounds, or solution which, when added to a system, changes pH to a specified, known value.
2. The ability a solution or system to resist change in pH if either an acid or a base is added.

**Buffering capacity**—A measurement of the amount of acid or base which can be added to a solution before the pH changes.

**Cation**—A positively charged ion (i.e.,  $NH_4^+$ ,  $Ca^{2+}$ ).

**Combination electrode**—An electrode composed of a reference half-cell and a sensing half-cell. The reference half-cell is the half of the electrode pair that maintains a constant potential

## Glossary, continued

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regardless of solution composition. The sensing half-cell develops a potential proportional to solution composition.

**Conditioning**—The process of preparing an electrode for use by soaking the electrode in a solution with a pH and ionic strength similar to the sample. Conditioning allows the formation of the hydrated layer, necessary for accurate measurements.

**Decade**—Any two standards with a concentration ratio of 10. For example:

$$\frac{\text{Concentration of the higher Standard}}{\text{Concentration of the lower Standard}} = 10$$

**Dilution factor**—A numerical value by which results must be multiplied in order to obtain the actual value of the sample. For example, if 1 mL of sample is diluted to 10 mL, then the result obtained must be multiplied by 10 to obtain the value for the sample before dilution.

**Electrolyte**—A solution made of dissolved ions that is used to facilitate electrical conductance and ionic transport. The composition is usually potassium chloride (KCl), sodium chloride (NaCl), ammonium chloride (NH<sub>4</sub>Cl), or ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>).

**Free-flowing reference junction**—The point on the electrode where reference gel is freely dispensed without obstruction by frits or other materials.

**Hydrated layer**—A layer that forms at the glass/liquid interface. Chemically similar to the sample being measured (especially in samples of low ionic strength), the formation characteristics of this layer depend upon the type of glass, the age of the glass, the previous usage history of the glass, the temperature and ionic strength of the aqueous solution, etc.

**Inert**—Does not react with other substances.



**Ion**—An atom, group of atoms or molecule that is electrically charged as the result of gaining or losing electrons. An ion resulting from the gain of electrons becomes negative (anion), while an ion resulting from the loss of electrons becomes positive (cation).

**Ionic strength**—A measure of the concentration of any ion in solution, usually expressed in moles per liter.

**Occasional use**—Infrequent use where the probe is subjected to test conditions just long enough to obtain a proper reading.

**pH**—A relative numerical measurement of the acidic, neutral, or alkali nature of a solution or system. Mathematically defined as the negative log of the hydrogen ion concentration.

**Potential**—The capacity of a system to perform work. When two ions of opposite charge are separated by a distance, there is a potential developed from the tendency of the ions to come back together. Each ion exerts work to come back together. The amount of work needed by each ion to come back together is the potential.

**Reference element**—A silver wire coated with silver chloride, this element develops a constant potential when immersed in an electrolyte such as potassium chloride.

**Reference half-cell**—Provides a constant voltage against which the pH dependent voltage from the sensing half-cell is compared.

**Reference junction**—The point on the electrode where reference gel is dispensed.

**Routine use**—Typical use following regular, frequent routines, but not continuous as with an in-line monitoring process.

**Salt**—An ionic compound.

**Sensing half-cell**—Provides a voltage proportional to the concentration of a specific ion in solution.

**Siemen**—The unit of conductivity equivalent to mho ( $\text{ohm}^{-1}$ ). Conductivity is often expressed as microSiemens per centimeter ( $\mu\text{S}/\text{cm}$ ) and milliSiemens per centimeter ( $\text{mS}/\text{cm}$ ) and it is a measure of how readily a sample conducts electricity. More concentrated solutions conduct more electricity and have higher conductivity.

**Sodium error (alkaline error)**—Occurs in strongly alkaline solutions, generally greater than 13 pH, when concentrations of  $\text{H}^+$  are low, and small, positively charged ions such as  $\text{Na}^+$  generate potential differences across the pH glass membrane. These differences can result in measurement errors between -0.5 and -1.0 pH.



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