pH

USEPA Electrode Method

Method 8156

pH electrode

Scope and application: For drinking water[1], wastewater[2] and process water.

[1] Based on Standard Method 4500-H+B, ASTM Method D1293-95 and USEPA Method 150.1
[2] Based on Standard Method 4500-H+B, ASTM Method D1293-84(90)/(A or B) and USEPA Method 150.1

Test preparation

Instrument specific information

This procedure is applicable to the meters and probes that are shown in Table 1. Procedures for other meters and probes can be different.

Table 1 Instrument-specific information

Meter	Probe
HQ1100 and HQ11d portable one input, pH/ORP HQ4100, HQ2100 and HQ30d portable one input, multi-parameter HQ4200, HQ2200 and HQ40d portable two input, multi-parameter HQ4300 portable three input, multi-parameter HQ411d benchtop one input, pH/mV HQ430d benchtop one input, multi-parameter HQ440d benchtop two input, multi-parameter SL1000 Multi-Port Portable Parallel Analyzer (PPA) SL250 Single-Port Portable Parallel Analyzer (PPA)	Intellical PHC101, PHC201, PHC281 or PHC301 pH
Sension+ MM156 portable pH/EC/DO	Sension+ 5049 multi-parameter
Sension+ pH1 portable pH Sension+ MM110 portable pH/ORP Sension+ MM150 portable pH/ORP/EC	Sension+ 5050T, 5051T or 5052T combination pH Sension+ 5045, 5048 or 5059 multi-parameter
Sension+ pH3 lab pH Sension+ pH31 GLP lab pH Sension+ MM340 lab two input, pH/mV/ISE Sension+ MM374 lab two input, pH/mV/EC/ISE Sension+ MM378 lab two input, pH/ISE/EC/DO	Sension+ 5010T, 5011T, 5014T or 5021T combination pH

Before starting

Refer to the meter documentation for meter settings and operation. Refer to probe documentation for probe preparation, maintenance and storage information.
Prepare the probe before initial use. Refer to probe documentation.
When an Intellical probe is connected to an HQ meter or an HQd meter, the meter automatically identifies the measurement parameter and is prepared for use.
When an Intellical probe is connected to an SL250 or SL1000, the instrument automatically identifies the measurement parameter and is prepared for use.
Condition the electrode for the best response time. To condition the electrode, soak the electrode for several minutes in a solution that has almost the same pH and ionic strength as the sample.
Calibrate the probe before initial use. Refer to Calibration procedure on page 3.
For rugged electrodes, it may be necessary to remove the shroud before measurement and calibration.

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Air bubbles under the sensor tip can cause slow response or measurement errors. To remove the bubbles, carefully shake the probe.
To save data automatically, set the measurement mode to Press to Read or Interval. When the measurement mode is Continuous, select Store to save data manually.
Rinse the electrode between measurements to prevent contamination.
Keep the electrode in a pH storage solution when not in use. Refer to the probe documentation.
Review the Safety Data Sheets (MSDS/SDS) for the chemicals that are used. Use the recommended personal protective equipment.
Dispose of reacted solutions according to local, state and federal regulations. Refer to the Safety Data Sheets for disposal information for unused reagents. Refer to the environmental, health and safety staff for your facility and/or local regulatory agencies for further disposal information.
This procedure is specified for the HQ meters and HQd meters. The Sension+ meters can be used, but the menus and navigation will be different.

Items to collect

Description	Quantity
Beaker or sample containers	3
Wash bottle with deionized water	1
pH buffers (4.0, 7.0, 10.0)	3

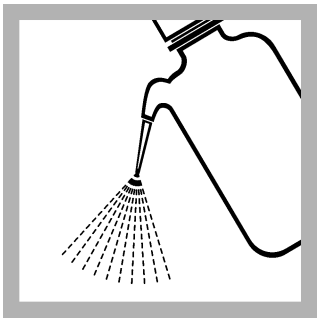
Refer to Consumables and replacement items on page 5 for order information.

Sample collection

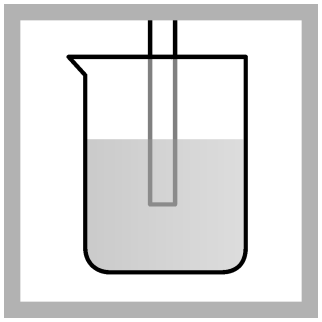
- Analyze the samples immediately. The samples cannot be preserved for later analysis.
- Collect samples in clean glass or plastic bottles.

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Test procedure

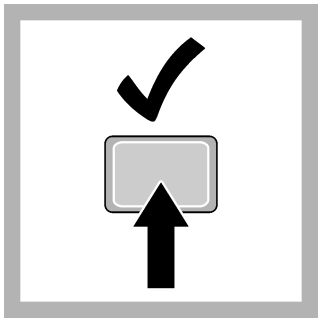


1. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

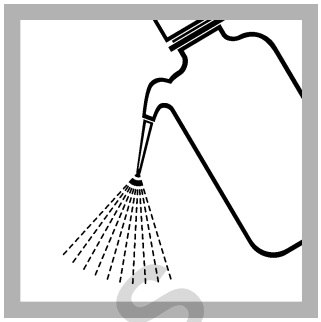


2. Laboratory test: Put the probe in a beaker that contains the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip. Stir the sample at a slow to moderate rate.
Field test: Put the probe in the sample. Move the probe up and down to remove bubbles from the electrode.

Make sure to put the temperature sensor fully in the sample.

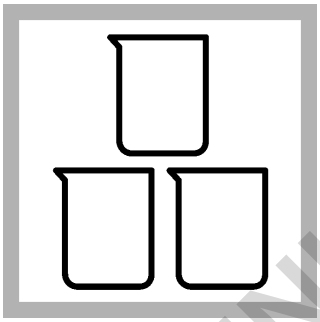


3. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.

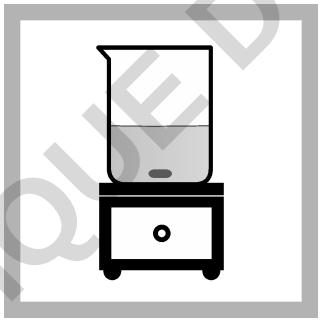


4. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

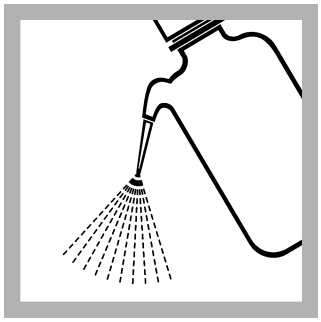
Calibration procedure



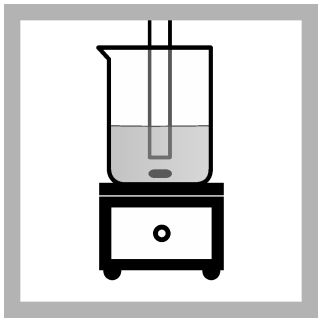
1. Prepare two or three fresh buffer solutions in separate beakers. If two buffers are used, use a 7.0 and a 4.0 or a 7.0 and a 10.0 pH buffer solution.



2. Add a stir bar and put the beaker on a magnetic stirrer. Stir at a moderate rate.

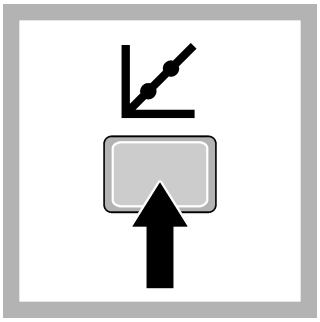


3. Rinse the probe with deionized water. Dry the probe with a lint-free cloth.

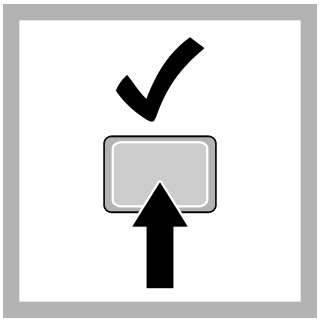


4. Put the probe in the solution. Do not let the probe touch the stir bar, bottom or sides of the container. Remove the air bubbles from under the probe tip.

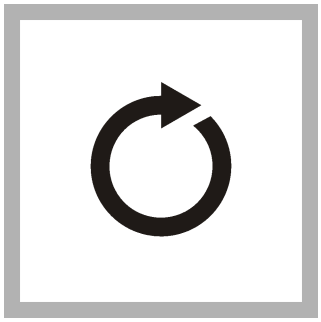
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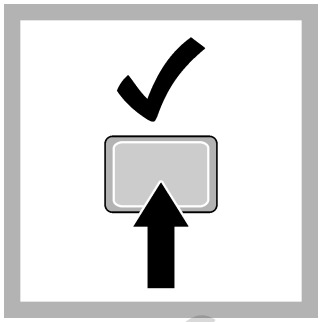
5. Push **Calibrate**. The standard solution value is shown.



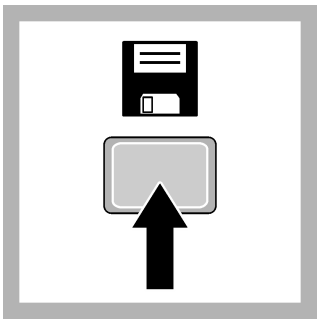
6. Push **Read**. A progress bar is shown. When the measurement is stable, the lock icon is shown.



7. Measure the remaining buffer solutions.



8. Push **Done**. A calibration summary is shown when the minimum number of calibration standards are measured.



9. Push **Store** to accept the calibration.

Low ionic strength or high-purity water measurements

NOTICE

Do not keep the probe in LIS samples for a long period of time because this can decrease the probe life. Put the probe in electrode storage solution or 3 M KCl when LIS measurements are complete.

Low ionic strength (LIS) solutions have very low buffering capacity and absorb carbon dioxide from the air. When a sample absorbs carbon dioxide from the atmosphere, carbonic acid forms. Carbonic acid decreases the sample pH, which causes inaccurate readings. One solution to this problem is to measure the sample in a low volume, airtight sample chamber such as a low ionic strength chamber.

Use refillable or platinum series electrodes for measurement of pH in LIS or high purity waters.

Before an LIS sample is measured, condition the probe as follows:

1. Soak the probe in a solution equivalent to the sample in ionic strength and pH for 10 to 15 minutes.
2. Rinse the probe with deionized water.
3. Dry the probe with a soft paper towel.

Between measurements, keep the probe in the sample or a neutral LIS solution (e.g., tap water) for a maximum of 2 hours.

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Interferences

The sodium error is low but increases at pH values that are higher than pH 11. The acid error is negligible. Refer to the electrode or the meter documentation.

Accuracy check

Slope test

The electrode operation is satisfactory when the calibration slope is within the specified range (typically –58 mV (±3) at 25 °C).

Calibration accuracy

Measure the pH of a fresh buffer solution. A calibration is satisfactory when the measured pH value agrees with the known pH value of the buffer solution.

Clean the probe

Clean the probe when:

- Drifting/inaccurate readings occur as a result of contamination on the sensing element or incorrect storage conditions.
- Slow response time occurs as a result of contamination on the sensing element.
- The slope is out of range as a result of contamination on the sensing element.

For general contamination, complete the steps that follow.

1. Rinse the probe with deionized water. Blot dry with a lint-free cloth.
2. Soak the glass bulb for 12 to 16 hours in Hach Electrode Cleaning Solution.
3. Rinse or soak the probe for 1 minute in deionized water.
4. Soak the probe in pH 4 buffer for up to 20 minutes, then rinse with deionized water.
5. Blot dry with a lint-free cloth.
6. If harsh contaminants are attached to the probe, polish the probe tip with a soft cloth or cotton swab to remove the contaminants.
7. Soak for up to 20 minutes in pH 4 buffer, then rinse with deionized water.

Method performance

The accuracy of the measurements is dependent on many factors that are related with the overall system, which includes the meter, the probe and calibration solutions. Refer to the meter or probe documentation for more information.

Summary of method

A combination pH electrode develops a potential at the glass/liquid interface. At a constant temperature, this potential varies linearly with the pH of the solution.

The pH is 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 sample pH can change when carbon dioxide is absorbed from the atmosphere. In water that has a high conductivity, the buffer capacity is typically high and the pH does not change much.

Consumables and replacement items

HQ meters, PPA, HQd meters and probes

Description	Unit	Item no.
HQ1110 portable one input, pH/ORP meter	each	LEV015.53.1110A
HQ2100 portable one input, multi-parameter meter	each	LEV015.53.2100A
HQ2200 portable two input, multi-parameter meter	each	LEV015.53.2200A
HQ4100 portable one input, multi-parameter meter	each	LEV015.53.4100A
HQ4200 portable two input, multi-parameter meter	each	LEV015.53.4200A
HQ4300 portable three input, multi-parameter meter	each	LEV015.53.4300A

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HQ meters, PPA, HQd meters and probes (continued)

Description	Unit	Item no.
HQ411d benchtop one input, pH/mV meter	each	HQ411D
HQ430d benchtop one input, multi-parameter meter	each	HQ430D
HQ440d benchtop two input, multi-parameter meter	each	HQ440D
SL1000 Multi-Port Portable Parallel Analyzer (PPA)	each	9430000
SL250 Single-Port Portable Parallel Analyzer (PPA)	each	9430250
Intellical pH gel probe, standard with 1 m cable	each	PHC10101
Intellical pH gel probe, standard with 3 m cable	each	PHC10103
Intellical pH gel probe, rugged with 5 m cable	each	PHC10105
Intellical pH gel probe, rugged with 10 m cable	each	PHC10110
Intellical pH gel probe, rugged with 15 m cable	each	PHC10115
Intellical pH gel probe, rugged with 30 m cable	each	PHC10130
Intellical pH gel probe, standard with 1 m cable	each	PHC20101
Intellical pH gel probe, standard with 3 m cable	each	PHC20103
Intellical pH gel probe, ultra with 1 m cable	each	PHC28101
Intellical pH gel probe, ultra with 3 m cable	each	PHC28103
Intellical pH liquid probe, standard with 1 m cable	each	PHC30101
Intellical pH liquid probe, standard with 3 m cable	each	PHC30103

Sension+ meters and probes

Description	Unit	Item no.
Sension+ pH3 lab pH meter	each	LPV2010T.97.002
Sension+ pH31 GLP lab pH meter	each	LPV2110T.97.002
Sension+ MM340 lab two input, pH/mV/ISE meter	each	LPV2200.97.0002
Sension+ MM374 lab two input, pH/mV/EC/ISE meter	each	LPV4110.97.0002
Sension+ MM378 lab two input, pH/ISE/EC/DO meter	each	LPV4130.97.0002
Sension+ 5010T combination pH probe	each	LZW5010T.97.002
Sension+ 5011T combination pH probe	each	LZW5011T.97.002
Sension+ 5014T combination pH probe	each	LZW5014T.97.002
Sension+ 5021T combination pH probe	each	LZW5021T.97.002
Sension+ 5050T combination pH probe	each	LZW5050T.97.002
Sension+ 5051T combination pH probe	each	LZW5051T.97.002
Sension+ 5052T combination pH probe	each	LZW5052T.97.002
Sension+ 5045 multi-parameter probe	each	LZW5045.97.0002
Sension+ 5048 multi-parameter probe	each	LZW5048.97.0002
Sension+ 5049 multi-parameter probe	each	LZW5049.97.0002
Sension+ 5059 multi-parameter probe	each	LZW5059.97.0002

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Recommended standards

Description	Unit	Item no.
pH 4.01 buffer solution, Singlet one-use packets, 20 mL each	20/pkg	2770020
pH 7.00 buffer solution, Singlet one-use packets, 20 mL each	20/pkg	2770120
pH 10.01 buffer solution, Singlet one-use packets, 20 mL each	20/pkg	2770220
pH 4.01 and pH 7.00 buffer solution kit, Singlet one-use packets, 20 mL each	2 x 10/pkg	2769920
pH 7.00 and 10.01 buffer solution kit, Singlet one-use packets, 20 mL each	2 x 10/pkg	2769820
pH color-coded buffer solution kit (NIST), 500 mL, includes:	1	2947600
pH 4.01 ± 0.02 pH buffer (NIST)	500 mL	2283449
pH 7.00 ± 0.02 pH buffer (NIST)	500 mL	2283549
pH 10.01 ± 0.02 pH buffer (NIST)	500 mL	2283649
Powder pillows:		
pH 4.01 ± 0.02 pH buffer powder pillow (NIST)	50/pkg	2226966
pH 7.00 ± 0.02 pH buffer powder pillow (NIST)	50/pkg	2227066
pH 10.01 ± 0.02 pH buffer powder pillow (NIST)	50/pkg	2227166
Radiometer Analytical (IUPAC Series certified pH standards):		
pH 1.679 ± 0.010 at 25 °C (77 °F)	500 mL	S11M001
pH 4.005 ± 0.010 at 25 °C (77 °F)	500 mL	S11M002
pH 6.865 ± 0.010 at 25 °C (77 °F)	500 mL	S11M003
pH 7.000 ± 0.010 at 25 °C (77 °F)	500 mL	S11M004
pH 9.180 ± 0.010 at 25 °C (77 °F)	500 mL	S11M006
pH 10.012 ± 0.010 at 25 °C (77 °F)	500 mL	S11M007
pH 12.45 ± 0.05 at 25 °C (77 °F)	500 mL	S11M008
pH buffer 1.09, technical	500 mL	S11M009
pH buffer 4.65, technical	500 mL	S11M010
pH buffer 9.23, technical	500 mL	S11M011

Accessories

Description	Unit	Item no.
Beaker, polypropylene, 50 mL, low form	each	108041
Beaker, polypropylene, 100-mL	each	108042
Bottle, wash, 500 mL	each	62011
Stir bar, magnetic, 2.2 x 0.5 cm (7/8 x 3/16 in.)	each	4531500
Stirrer, electromagnetic, 120 VAC, with electrode stand	each	4530001
Stirrer, electromagnetic, 230 VAC, with electrode stand	each	4530002
Sample bottle with screw-top cap, polypropylene, 500-mL	each	2758101
Water, deionized	4 L	27256

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