Handbook

Thermo Scientific

pH Measurement Handbook

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pH Theory

The term pH is derived from a combination of "p" for the word power and "H" for the symbol of the element Hydrogen. Together the meaning is the power of hydrogen. pH serves as a convenient way to compare the relative acidity or alkalinity of a solution at a given temperature. A pH of 7 describes a neutral solution because the activities of hydrogen and hydroxide ions are equal. When the pH is below 7, the solution is described as acidic because the activity of hydrogen ion is greater than that of hydroxide ion. A solution is more acidic as the hydrogen ion activity increases and the pH value decreases. Conversely, when the pH is above 7, the solution is described as basic (or alkaline) because the activity of hydroxide ion is greater than that of hydrogen ion.

pH Electrode Theory

pH electrode measurements are made by comparing the readings in a sample with the readings in standards whose pH has been defined (buffers). When a pH sensing electrode comes in contact with a sample, a potential develops across the sensing membrane surface and that membrane potential varies with pH. A reference electrode provides a second, unvarying potential to quantitatively compare the changes of the sensing membrane potential. Combination pH electrodes are composed of a sensing electrode with the reference electrode built into the same electrode body. Combination electrodes provide the same selectivity and response as a half-cell system, but offer the convenience of working and maintaining only one electrode. A meter serves as the readout device and calculates the difference between the reference electrode and sensing electrode potentials in millivolts. The millivolts are then converted to pH units and shown on the meter display. The sample or standard solution is the final component of the system.

Electrode behavior is described by the Nernst equation: $\mathbf{E = E_0 + (2.3\ RT/nF)\ log\ aH^+}$

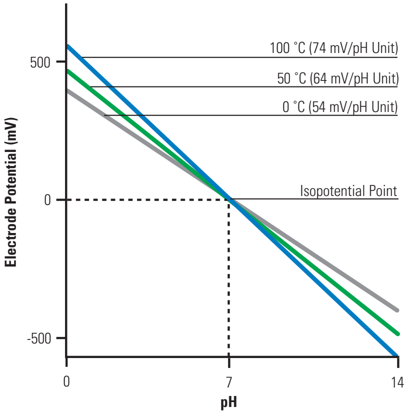
E is the measured potential from the sensing electrode, E_0 is related to the potential of the reference electrode, (2.3 RT/nF) is the Nernst factor and log aH+ is the pH. The Nernst factor, 2.3 RT/nF, includes the Gas Law constant (R), Faraday's constant (F), the temperature in degrees Kelvin (T) and the charge of the ion (n). For pH, where n = 1, the Nernst factor is 2.3 RT/F. Since R and F are constants, the factor and therefore electrode behavior is dependent on temperature.

The electrode slope is a measure of the electrode response to the ion being detected and is equivalent to the Nernst factor. When the temperature is 25 °C, the theoretical Nernst slope is 59.16 mV/pH unit. Thermo Scientific pH meters display the slope as a percentage of the theoretical value. For example, a 98.5 % slope is equivalent to a slope of 58.27 mV/pH unit for a two-point calibration. The pH meter detects the pH sensing bulb signal, reference signal and temperature signal and uses these values to calculate the pH using the Nernst equation. Thermo Scientific pH meters contain pH versus temperature values for commonly used buffers. This allows the meter to recognize a particular pH buffer and calibrate with the correct buffer value at the measured temperature.

pH versus Temperature Theory

The most common cause of error in pH measurements is temperature. Temperature variations can influence pH for the following reasons:

- The electrode slope will change with variations in temperature.
- Buffer and sample pH values will change with temperature.
- Measurement drift can occur when the internal elements of the pH and reference electrodes are reaching thermal equilibrium after a temperature change.



- When the pH electrode and temperature probe are placed into a sample that varies significantly in temperature, the measurements can drift because the temperature response of the pH electrode and temperature probe may not be similar and the sample may not have a uniform temperature, so the pH electrode and temperature probe are responding to different environments.

Electrode slope changes can be compensated for by using an automatic temperature compensation (ATC) probe or a Thermo Scientific™ Orion™ Triode™ electrode which has an ATC probe incorporated into the body of the electrode. Thermo Scientific™ pH meters calculate the electrode slope based on the measured temperature of the pH buffers. The meter will automatically adjust the pH buffer value to the actual pH of the buffer at the measured temperature.

The pH values of buffers and samples will change with variations in temperature because of their temperature dependent chemical equilibria. The pH electrode should be calibrated with buffers that have known pH values at different temperatures. Since pH meters are unable to correct sample pH values to a reference temperature, due to the unique pH versus temperature relationship of each sample, the calibration and measurements should be performed at the same temperature and sample pH values should be recorded with the sample temperature.

Nominal pH Value at 25 °C	0 °C	5 °C	10 °C	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
1.68	1.67	1.67	1.67	1.68	1.68	1.69	1.71	1.72	1.74	1.77	1.79
4.01	4.00	4.00	4.00	4.00	4.02	4.03	4.06	4.09	4.12	4.16	4.21
6.86	6.98	6.95	6.92	6.87	6.85	6.84	6.83	6.84	6.85	6.86	6.88
7.00	7.11	7.08	7.06	7.01	6.98	6.97	6.96	6.97	7.00	7.03	7.08
9.18	9.46	9.40	9.33	9.23	9.14	9.07	9.01	8.96	8.92	8.89	8.85
10.01	10.32	10.25	10.18	10.06	9.97	9.89	9.83	9.79	9.78	9.78	9.80
12.46	13.47	13.24	13.03	12.64	12.29	11.99	11.73	11.50	11.30	11.13	10.98

pH Electrode Selection Guide

The types of available electrodes, the desired electrode features and the compatibility of the electrode with the sample are all determining factors in selecting the right pH electrode. The following section provides the information needed to select the best pH electrode for your applications. The pH electrodes are available with a glass or epoxy body and a variety of electrode body styles, fill types, references, junctions and connectors that suit your application. Other factors to consider when selecting a pH electrode include:

- The reference junction should provide a stable and reproducible reading under a wide variety of sample conditions. Thermo Scientific electrodes include a large selection of reference junctions and filling solutions that are designed to provide fast and reliable readings in all types of samples. Electrodes with a Thermo Scientific™ Sure-Flow™ reference junction can be used in a variety of samples, including difficult samples such as dirt, colloids, sludge and viscous material.

- The electrode filling solution should not interfere with the electrode measurements. Electrodes with a double junction reference prevent silver ions from coming in contact with the sample, which is key when measuring samples that contain silver-binding agents such as TRIS buffer, proteins or sulfides. Refillable Thermo Scientific™ Orion™ ROSS Ultra™ and Thermo Scientific™ Orion™ ROSS™ electrodes do not contain any silver and allow the operator to modify the outer filling solution. This is useful when the regular filling solution contains ions that interfere or react with the sample that is being measured.

- The filling solution should flow freely with no fouling or clogging of the junction by the sample. The Sure-Flow reference junction on many Thermo Scientific pH electrodes improves the electrode performance by allowing a constant flow of filling solution into the sample. The enhanced flow rate produces stable reference potentials for faster response and better stability. In addition, pressing on the electrode cap flushes the reference, which allows for easy cleaning and refilling of the electrode. Thermo Scientific™ AquaPro™ pH electrodes incorporate a high-performance polymer that isolates the silver internal reference from the sample. These low maintenance pH electrodes offer a rapid response due to their open junction design, even in dirty or viscous samples.

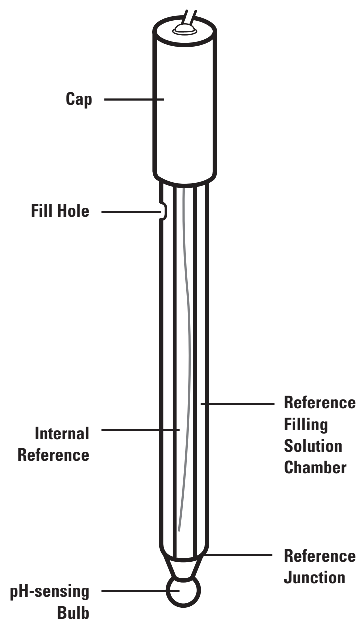


Figure 1 – Typical pH Electrode Components

Thermo Scientific pH Electrode Families

ROSS Ultra Premium pH Electrodes

The best of the best! The fastest response, highest accuracy and best reproducibility that you can get with a pH electrode – plus a 1½ to 2 year warranty.

ROSS Ultra pH/ATC Triode™

These electrodes include a built-in temperature sensor to measure both pH and temperature with one electrode, minimizing the amount of required sample.

ROSS Premium pH Electrodes

Precise pH measurements with unmatched stability, reliability and rapid response regardless of temperature or sample composition.

ROSS Micro pH Electrode

Measure samples as small as 15 µL in 384 well plates. Use with the Thermo Scientific™ Orion™ VERSA STAR™ LogR™ meter to take pH and temperature measurements utilizing LogR technology.

No Cal pH Electrodes

The world's first pH electrode that does not require calibration! No Cal pH electrodes maintain their calibration to 0.1 pH units for one year when properly stored and maintained.

AquaPro Professional pH Electrodes

Low maintenance, clog resistant double junction electrodes with an extended life and fast response.

Standard Ag/AgCl pH Electrodes

A large variety of quality electrodes for a wide range of applications. Includes specialty pH electrodes for unique or challenging pH measurements.

Green pH Electrodes

These environmentally friendly electrodes contain no lead, mercury or other hazardous substance, which allows for easy and hassle-free electrode disposal and meets all the requirements of RoHS.

Micro Ag/AgCl pH Electrodes

These pH electrodes measure samples as small as 0.5 µL in containers as small as 384 well plates.

Double Junction pH Electrodes

Isolated Ag/AgCl reference system that prevents silver from coming in contact with the sample and is great for measuring TRIS buffer, sulfide and protein samples. Includes the Thermo Scientific™ KNIpHE™ pH electrode within a stainless blade for measuring meat, cheese and sludge samples.

Economy pH Electrodes

Good performance, value-priced, durable and low maintenance gel-filled pH electrodes.

ATC Probes

Automatic temperature compensation probes measure sample temperatures and adjust pH measurements by correcting the electrode slope according to the measured temperature.

pH Electrode Features

pH Electrode Styles

Standard Size

12 mm electrode diameter for use in a wide variety of sample sizes

Semi-micro

6 to 8 mm electrode diameter for sample sizes down to 200 µL

Micro

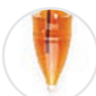
1 to 5 mm electrode diameter for samples as small as 0.5 µL and containers as small as 384 well plates

Rugged Bulb

When glass is required, the extra durable pH bulb prevents breakage

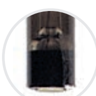
Spear Tip

For piercing solid or semi solid samples and measuring small volume samples



Flat Surface Tip

For measuring surfaces of solid or gel samples and measuring small volume samples



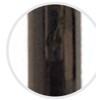
pH Electrode Body Materials

Glass Body

- Compatible with virtually any sample, including solvents
- Easy to clean

Epoxy Body

- Extremely durable and rugged to prevent breakage
- Value-priced



pH Electrode Junctions

Sure-Flow, Sleeve and Laser-Drilled Hole (Open)

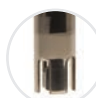
- Best junction for dirty, difficult samples
- Junction is clog-free and easy to clean
- Ideal for thick or viscous samples, compatible with all sample types

Ceramic and Glass Capillary

- Better junction for routine lab or field use
- Junction is high quality and durable
- Ideal for most applications and samples

Wick and Glass Fiber

- Good junction for routine lab or field use
- Junction used with rugged epoxy electrodes
- Ideal for aqueous samples



pH Electrode Fill Types

Refillable

- Easy maintenance, filling solution required
- Periodic filling and draining needed
- Long expected life span
- 0.01 to 0.02 pH precision
- Best response time
- 1 to 2 year warranty (6 months for Ag/AgCl micro electrodes)

Polymer Filled (Sealed)

- Low maintenance, no filling solution needed
- Sealed reference
- Easy to use, ideal for most applications
- 0.02 pH precision
- Better response time
- 1 year warranty

Gel Filled (Sealed)

- Low maintenance, no filling solution needed
- Sealed reference
- Easy to use, general purpose
- 0.05 to 0.1 pH precision
- Good response time
- 3 to 6 month warranty

pH Electrode References

ROSS Reference

- 0.01 pH precision
- Best measurement response time
- Ideal for TRIS, protein and sulfide samples
- Variety of body styles and types
- Refillable or gel design
- Best temperature response

Double Junction Ag/AgCl Reference

- 0.02 pH precision
- Better measurement response time
- Ideal for TRIS, protein and sulfide samples
- Variety of body styles and types
- Refillable, polymer or gel design
- Good temperature response

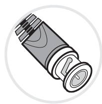
Single Junction Ag/AgCl Reference

- 0.02 to 0.1 pH precision
- Good measurement response time
- General purpose for everyday use
- Variety of body styles and types
- Refillable or gel design
- Good temperature response

pH Electrode Connectors

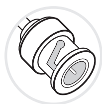
Waterproof BNC

Compatible with any pH meter that has a BNC input. Ensures a waterproof and secure connection with the Thermo Scientific™ Orion™ Star™ A series meters.



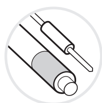
BNC

Compatible with any pH meter that has a BNC input



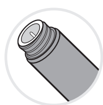
U.S. Standard

Compatible with older style meters that have a U.S. standard input.



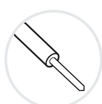
Screw Cap

Electrode can be connected to a variety of meter inputs using a separate cable.



Pin Tip

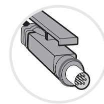
Compatible with meters that have a reference half-cell input.



ATC Probe Connectors

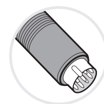
MiniDIN

Compatible with the Orion Star A, Thermo Scientific™ Orion™ DUAL STAR™ and VERSA STAR meters. and pH meters that have an 8 pin MiniDIN ATC input.



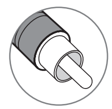
8 Pin DIN

Compatible with the Thermo Scientific™ Orion™ A+™ meters and pH meters that have an 8 pin DIN ATC input.



RCA

Compatible with Mettler Toledo™ pH meters that have an RCA input.



ATC Probe Ordering Information

Cat. No	Description
927005MD	Epoxy ATC probe, MiniDIN
927006MD	Glass ATC probe, MiniDIN
927007MD	Stainless steel ATC probe, MiniDIN
928007MD	Micro ATC probe with stainless steel 1 mm x 38 mm tip, MiniDIN
917005	Epoxy ATC probe, 8 Pin DIN
917007	Stainless steel ATC probe, 8 Pin DIN
927005	Epoxy ATC probe, 3.5 mm phono tip

Adapter Cable Ordering Information

Cat. No	Description
090032	U.S. standard meter to BNC pH electrode adapter
090033	BNC meter to U.S. standard pH electrode adapter
090034	E DIN meter to BNC pH electrode adapter
090035	LEMO miniature meter to BNC pH electrode adapter
91CBNC	BNC meter to screw cap pH electrode cable
91USCB	U.S. standard meter to screw cap combination pH electrode cable

pH Electrode Recommendations by Sample

	Electrode Recommendations
Biological/Pharmaceutical – TRIS buffer, proteins, enzymes	Electrodes should have a ROSS or double junction Ag/AgCl reference (no sample contact with silver)
Education/Student Use	Electrodes should have an epoxy body for added durability
Emulsions – Foods, cosmetics, oils	Electrodes should have a Sure-Flow or open junction to prevent the electrode from clogging
Emulsions – Petroleum products, paint	Electrodes should have a glass body that resists damage from the sample and a Sure-Flow or open junction to prevent the electrode from clogging
Flat Surfaces – Cheese, meat, agar	Electrodes should have a flat-surface tip and ROSS or double junction Ag/AgCl reference (no sample contact with silver)
Flat Surfaces – Paper	Electrodes should have a flat-surface tip
General Purpose – Most sample types	All electrodes are suitable for general purpose measurements
Harsh Environments – Field or plant use, rugged use	Electrodes should have an epoxy body for added durability and be polymer or gel filled for easy maintenance
High Ionic Strength – Acids, bases, brines, pH > 12 or pH < 2	Electrodes should have a Sure-Flow or open junction for better contact with the sample and more stable measurements
High Temperatures	Electrodes should have a ROSS reference for longer life and/or a quick flow junction for fast response
HF Samples	Electrodes should have a rugged or durable glass bulb and a double junction to protect the reference
Large Sample Sizes – Tall flasks	Electrodes should have a long body that fits the container
Low Ionic Strength – Treated effluent, deionized water, distilled water	Electrodes should be refillable for better contact with the sample and more stable measurements
Nonaqueous – Solvents, alcohols	Electrodes should have a glass body that resists damage from the sample and a Sure-Flow junction for better contact with the sample and more stable measurements
Semi-solids – Fruit, meat, cheese	Electrodes should have a spear tip for piercing samples and a ROSS or double junction Ag/AgCl reference
Small Sample Size – Micro-titer plates	Electrodes should have a small diameter that fits the container
Small Sample Size – NMR tubes	Electrodes should have a small diameter that fits the container
Small Sample Size – Test tubes, small flasks and beakers	Electrodes should have a small diameter that fits the container
Small Sample Size – TRIS buffer, proteins, sulfides	Electrodes should have a small diameter that fits the container and a ROSS or double junction Ag/AgCl reference
Titration	Electrodes should have a Sure-Flow or sleeve junction for better contact with the sample and more stable measurements
Viscous Liquids – Slurries, suspended solids sludges	Electrodes should have a Sure-Flow or open junction to prevent the electrode from clogging
Waters – Acid rain, boiler feed water, distilled water, rain water, well water	Electrodes should have a ROSS or double junction Ag/AgCl reference and be refillable for better contact with the sample
Waters – Drinking water, tap water	Electrodes should have an epoxy body for added durability
Waters – Wastewater, seawater	Electrodes should have a ROSS or double junction Ag/AgCl reference and have an epoxy body for added durability

pH Electrode Catalog Numbers by Sample

	ROSS Ultra	ROSS	AquaPro	Standard Ag/AgCl	Green	Micro Ag/AgCl	Double Junction	Economy
Biological/Pharmaceutical – TRIS buffer, proteins, enzymes	8102BNUWP, 8107BNUMD 8156BNUWP, 8157BNUMD 8302BNUMD, 8107BNURCA, 8157BNURCA, and 8302BNURCA	8102BN, 8104BN 815600, 8165BNWP 8172BNWP	9102AP 9104APWP 9107APMD 9156APWP	9165BNWP, 9172BNWP	GD9106BNWP GD9156BNWP		9102DJWP 9156DJWP	
Education/Student Use	8107BNUMD, 8156BNUWP 8157BNUMD, 8107BNURCA, 8157BNURCA	815600, 8165BNWP	9107APMD 9156APWP	9107BNMD, 9156BNWP, 9157BNMD	GS9106BNWP GD9106BNWP		9156DJWP	9106BNWP
Emulsions – Foods, cosmetics, oils		8165BNWP 8172BNWP	9104APWP 9107APMD	9165BNWP, 9172BNWP				
Emulsions – Petroleum products, paint		8172BNWP	9102AP 9104APWP	9172BNWP				
Flat Surfaces – Cheese, meat, agar	8135BNUWP	8135BN	9135APWP					
Flat Surfaces – Paper	8135BNUWP	8135BN	9135APWP	9167SC				913600
General Purpose – Most sample types	8102BNUWP, 8107BNUMD 8156BNUWP, 8157BNUMD 8302BNUMD, 8107BNURCA, 8157BNURCA, and 8302BNURCA	8102BN, 8104BN 815600, 8165BNWP 8172BNWP	9102AP 9104APWP 9107APMD 9156APWP	9102BNWP, 9107BNMD, 9156BNWP, 9157BNMD	GS9106BNWP GD9106BNWP GS9156BNWP GD9156BNWP		9102DJWP 9156DJWP	9106BNWP
Harsh Environments – Field or plant use, rugged use	8107BNUMD, 8107BNURCA		9107APMD 9156APWP	9107BNMD	GS9106BNWP GD9106BNWP		9156DJWP	9106BNWP
High Ionic Strength – Acids, bases, brines, pH > 12 or pH < 2		8165BNWP 8172BNWP	9104APWP 9107APMD 9102AP	9165BNWP 9172BNWP				
High Temperatures	8157BNUMD, 8102BNUMD, 8107BNUMD	8165BNWP, 8172BNWP		9165BNWP, 9172BNWP				
HF Samples	8302BNUMD	8172BNWP, 8104BN	9104APWP					
Large Sample Sizes – Tall flasks								912600
Low Ionic Strength – Treated effluent, deionized water, distilled water	8102BNUWP, 8156BNUWP 8157BNUMD, 8302BNUMD, 8157BNURCA and 8302BNURCA	8102BN, 815600 8165BNWP 8172BNWP		9165BNWP, 9172BNWP	GS9156BNWP GD9156BNWP		9102DJWP	
Nonaqueous – Solvents, alcohols		8172BNWP		9172BNWP				
Semi-solids – Fruit, meat, cheese		8163BNWP					9120APWP	
Small Sample Size – Micro-titer plates		8220BNWP				9810BN		
Small Sample Size – NMR tubes						9826BN		
Small Sample Size – Test tubes, small flasks and beakers	8103BNUWP, 8115BNUWP	8103BN, 8115BN 8175BNWP	9103APWP 9115APWP	9103BNWP		9810BN, 9826BN	9110DJWP	911600, 912600
Small Sample Size – TRIS buffer, proteins, sulfides	8103BNUWP, 8115BNUWP	8103BN, 8115BN 8175BNWP	9103APWP 9115APWP				9110DJWP	
Titration		8162SC, 8172BNWP, 8165BNWP						
Viscous Liquids – Slurries, suspended solids sludges		8165BNWP 8172BNWP	9104APWP 9107APMD	9165BNWP, 9172BNWP				
Waters – Acid rain, boiler feed water, distilled water, rain water, well water	8102BNUWP, 8156BNUWP 8157BNUMD, 8302BNUMD, 8157BNURCA and 8302BNURCA	8102BN, 815600 8165BNWP 8172BNWP		9165BNWP, 9172BNWP	GS9156BNWP GD9156BNWP		9102DJWP	
Waters – Drinking water, tap water	8156BNUWP, 8157BNUMD, 8157BNURCA	815600, 8165BNWP	9107APMD 9156APWP	9156BNWP, 9165BNWP	GS9106BNWP GD9106BNWP		9156DJWP	9106BNWP
Waters – Wastewater, seawater	8156BNUWP, 8157BNUMD, 8157BNURCA and 8302BNURCA	815600, 8165BNWP	9107APMD 9156APWP	9165BNWP	GD9106BNWP GD9156BNWP		9156DJWP	

pH Electrode Summary Table

Electrode Family	Cat. No.	pH Precision	Temperature Range	Body Type	Fill Solution Cat. No.	Special Features
ROSS Ultra	8102BNUWP	0.01	0 to 100 °C	Glass	810007	
	8103BNUWP	0.01	0 to 100 °C	Glass	810007	Semi-micro
	8104BNUWP	0.01	0 to 100 °C	Glass	810007	Rugged bulb
	8107BNUMD, 8107BNURCA	0.01	0 to 80 °C	Epoxy	Gel	pH/ATC Triode
	8115BNUWP	0.01	0 to 100 °C	Epoxy	810007	Semi-micro
	8135BNUWP	0.01	0 to 100 °C	Epoxy	810007	Flat surface
	8156BNUWP	0.01	0 to 100 °C	Epoxy	810007	
	8157BNUMD, 8157BNURCA	0.01	0 to 100 °C	Epoxy	810007	pH/ATC Triode
	8302BNUMD, 8302BNURCA	0.01	0 to 100 °C	Glass	810007	pH/ATC Triode
ROSS	8102BN	0.01	0 to 100 °C	Glass	810007	
	8103BN	0.01	0 to 100 °C	Glass	810007	Semi-micro
	8104BN	0.01	0 to 100 °C	Glass	810007	Rugged bulb
	8115BN	0.01	0 to 100 °C	Epoxy	810007	Semi-micro
	8135BN	0.01	0 to 100 °C	Epoxy	810007	Flat surface
	815600	0.01	0 to 100 °C	Epoxy	810007	
	8162SC	0.01	0 to 100 °C	Glass	810007	Sleeve junction
	8163BNWP	0.01	0 to 100 °C	Glass	810007	Spear tip
	8165BNWP	0.01	0 to 100 °C	Epoxy	810007	Sure-Flow
	8172BNWP	0.01	0 to 100 °C	Glass	810007	Sure-Flow
	8175BNWP	0.01	0 to 100 °C	Epoxy	810007	Semi-micro Sure-Flow
	8220BNWP	0.01	0 to 100 °C	Glass	810007	Micro, 3 x 40 mm tip
No Cal	5107BNMD	0.1	0 to 100 °C	Epoxy	510011	Calibration stable for 1 year, pH/ATC
AquaPro	9102AP	0.02	0 to 60 °C	Glass	Polymer	
	9103APWP	0.02	0 to 60 °C	Glass	Polymer	Semi-micro
	9104APWP	0.02	0 to 60 °C	Glass	Polymer	Rugged bulb
	9107APMD	0.02	0 to 60 °C	Epoxy	Polymer	pH/ATC Triode
	9115APWP	0.02	0 to 60 °C	Epoxy	Polymer	Semi-micro
	9135APWP	0.02	0 to 60 °C	Epoxy	Polymer	Flat surface
	9156APWP	0.02	0 to 60 °C	Epoxy	Polymer	

Electrode Family	Cat. No.	pH Precision	Temperature Range	Body Type	Fill Solution Cat. No.	Special Features
Standard Ag/AgCl	9102BNWP	0.02	0 to 90 °C	Glass	900011	
	9103BNWP	0.02	0 to 90 °C	Glass	900011	Semi-micro
	9104BNWP	0.02	0 to 90 °C	Glass	900011	Rugged bulb
	9107BNMD	0.02	0 to 80 °C	Epoxy	Gel	pH/ATC Triode
	9156BNWP	0.02	0 to 90 °C	Epoxy	900011	
	9157BNMD	0.02	0 to 90 °C	Epoxy	900011	pH/ATC Triode
	9162BNWP	0.02	0 to 90 °C	Glass	900011	Low resistance
	9163SC	0.02	0 to 90 °C	Glass	900011	Spear tip
	9165BNWP	0.02	0 to 100 °C	Epoxy	900011	Sure-Flow
	9166SC	0.02	0 to 90 °C	Glass	900011	Sleeve junction
	9167SC	0.02	0 to 90 °C	Glass	900011	Semi-micro flat surface
	9172BNWP	0.02	0 to 100 °C	Glass	900011	Sure-Flow
Green	GS9106BNWP	0.05	0 to 90 °C	Epoxy	Gel	
	GS9156BNWP	0.02	0 to 90 °C	Epoxy	900011	
	GD9106BNWP	0.02	0 to 90 °C	Epoxy	Gel	Double junction
	GD9156BNWP	0.02	0 to 90 °C	Epoxy	910008-WA	Double junction
Micro Ag/AgCl	9810BN	0.02	0 to 80 °C	Glass	900011	1.3 x 37 mm tip
	9826BN	0.02	0 to 80 °C	Glass	900011	For NMR tubes
	9863BN	0.02	0 to 80 °C	S. Steel	900011	Needle tip
Double Junction	9102DJWP	0.02	0 to 60 °C	Glass	910008-WA	
	9110DJWP	0.02	0 to 60 °C	Glass	910008-WA	Semi-micro
	9120APWP	0.02	0 to 60 °C	S. Steel	910008-WA	KNIpHE blade for meat samples
	9156DJWP	0.02	0 to 60 °C	Epoxy	Gel	
Economy	9106BNWP	0.05	0 to 80 °C	Epoxy	Gel	
	911600	0.1	0 to 80 °C	Epoxy	Gel	Semi-micro
	912600	0.1	0 to 80 °C	Epoxy	Gel	For long flasks
	913600	0.1	0 to 80 °C	Epoxy	Gel	Flat surface

pH Electrode Operation Guide

pH Electrode Preparation

The following is a general procedure for preparing most pH electrodes. Refer to the electrode user guide or instruction manual for an electrode-specific preparation procedure.

1. Remove the protective shipping cap, sleeve or bottle from the electrode pH-sensing bulb and save the cap, sleeve or bottle for storage. If the electrode has a storage bottle covering the pH-sensing bulb, unscrew the storage bottle cap before removing the electrode from the storage bottle.
2. Clean any salt deposits from the electrode exterior by rinsing it with distilled water.
3. If the electrode is refillable, uncover the fill hole and add the appropriate filling solution 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 fill hole should be open whenever the electrode is in use.
4. Gently shake the electrode downward (similar to a clinical thermometer) to remove any air bubbles that may be trapped inside the electrode.
5. Soak the electrode in ROSS pH electrode storage solution, Cat. No. 810001, or standard pH electrode storage solution, Cat. No. 910001, for at least 30 minutes. The ROSS storage solution is recommended for enhanced electrode performance.
6. Connect the electrode to the meter.
7. Select at least two pH buffers that bracket the expected sample pH and will be used during the calibration of the pH electrode.

Thermo Scientific pH Buffers and Storage Solutions

Cat. No.	Description
810001	ROSS pH electrode storage solution, 475 mL bottle
810199	ROSS All-in-one pH buffer kit, includes one 475 mL bottle each of 4.01, 7.00 and 10.01 buffer, one 475 mL bottle of ROSS pH electrode storage solution, one 60 mL bottle of pH electrode cleaning solution and one electrode storage bottle.
910199	All-in-one pH buffer kit, includes one 475 mL bottle each of 4.01, 7.00 and 10.01 buffer, one 475 mL bottle of standard pH electrode storage solution and one electrode storage bottle
910168	pH 1.68 buffer, 475 mL bottle
9116860	pH 1.68 buffer, 5 x 60 mL bottles
910104	pH 4.01 buffer, 475 mL bottle
910460	pH 4.01 buffer, 5 x 60 mL bottles
910425	pH 4.01 buffer, 25 x 15 mL individual buffer pouches
910105	pH 5.00 buffer, 475 mL
910686	pH 6.86 buffer, 475 mL bottle
916860	pH 6.86 buffer, 5 x 60 mL bottles
910107	pH 7.00 buffer, 475 mL bottle
910760	pH 7.00 buffer, 5 x 60 mL bottles
910725	pH 7.00 buffer, 25 x 15 mL individual buffer pouches
910918	pH 9.18 buffer, 475 mL bottle
9191860	pH 9.18 buffer, 5 x 60 mL bottles
910110	pH 10.01 buffer, 475 mL bottle
911060	pH 10.01 buffer, 5 x 60 mL bottles
911025-WA	pH 10.01 buffer, 25 x 15 mL individual buffer pouches
910112	pH 12.46 buffer, 475 mL bottle
911260-WA	pH 12.46 buffer, 5 x 60 mL bottles
910001	Standard pH electrode storage solution, 475 mL bottle

pH Electrode Calibration

Calibration Recommendations

- Always pour fresh pH buffers into clean beakers for calibration. Choose buffers that are one to four pH units apart.
- Check the electrode slope daily by performing at least a two buffer calibration. The slope should be 92 to 102 % (54.43 to 60.34 mV per pH unit).
- If the electrode is refillable, uncover the fill hole during calibration to ensure a uniform flow of filling solution. The filling solution level inside of the electrode must be at least one inch above the buffer solution level.
- The buffer solution level must be above the pH electrode reference junction when the electrode is immersed in the buffer.
- Between buffers, rinse the electrode with distilled water and then with the next buffer. To reduce the chance of error due to polarization, avoid rubbing or wiping the electrode bulb. Use a lint-free tissue and gently blot the bulb.
- Use the Orion Star stirrer probe, Cat. No. 096019, or a magnetic stir plate and stir bar to stir all buffers and samples at a moderate, uniform rate. The stirrer probe can be used with the Orion Star A, Dual Star and Versa Star benchtop meters.
- If using a magnetic stir plate, place a piece of insulating material, such as polystyrene foam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.
- Handle the micro pH electrodes with care. Do not touch the pH bulb and stem against the bottom or walls of the sample containers.

Nominal pH Value at 25 °C	0 °C	5 °C	10 °C	20 °C	30 °C	40 °C	50 °C	60 °C	70 °C	80 °C	90 °C
1.68	1.67	1.67	1.67	1.68	1.68	1.69	1.71	1.72	1.74	1.77	1.79
4.01	4.00	4.00	4.00	4.00	4.02	4.03	4.06	4.09	4.12	4.16	4.21
6.86	6.98	6.95	6.92	6.87	6.85	6.84	6.83	6.84	6.85	6.86	6.88
7.00	7.11	7.08	7.06	7.01	6.98	6.97	6.96	6.97	7.00	7.03	7.08
9.18	9.46	9.40	9.33	9.23	9.14	9.07	9.01	8.96	8.92	8.89	8.85
10.01	10.32	10.25	10.18	10.06	9.97	9.89	9.83	9.79	9.78	9.78	9.80
12.46	13.47	13.24	13.03	12.64	12.29	11.99	11.73	11.50	11.30	11.13	10.98

Table A: pH Values of Buffers at Various Temperatures

Three Buffer Calibration Procedure

This procedure is recommended for precise measurements. Refer to the meter user guide for detailed instructions on how to perform a pH calibration using your meter.

1. Verify that the pH electrode was prepared correctly and connect the electrode to the meter.
2. Select three pH buffers that bracket the expected sample pH. It is recommended that one buffer be near the electrode isopotential point (pH 7) and the other buffers be near the expected sample pH and one to four pH units apart (for example, pH 4 and pH 10). The pH buffers should be at the same temperature as the sample. If the buffers and samples are at varying temperatures, temperature compensation is recommended.
3. Pour about 30 mL of each pH buffer into 50 mL beakers and proceed with the calibration immediately.
4. Start the calibration on the meter.
5. Rinse the electrode with de-ionized water and gently blot excess drops with a lint-free tissue.
6. Place the electrode into the first buffer, so the electrode tip and junction are fully immersed in the buffer, and stir the buffer at a moderate, uniform rate.
7. When the reading is stable, accept the buffer value using the meter's automatic buffer recognition feature or manually enter the value of the pH buffer at its measured temperature. Table A provides pH values for Thermo Scientific Orion buffers at various temperatures.
8. Rinse the electrode with de-ionized water and **gently blot excess drops** with a lint-free tissue.
9. Place the electrode into the second buffer, so the electrode tip and junction are fully immersed in the buffer, and stir the buffer at a moderate, uniform rate.
10. When the reading is stable, accept the buffer value using the meter's automatic buffer recognition feature or manually enter the value of the pH buffer at its measured temperature. Rinse the electrode with de-ionized water and **gently blot excess drops** with a lint-free tissue.
11. Place the electrode into the third buffer, so the electrode tip and junction are fully immersed in the buffer, and stir the buffer at a moderate, uniform rate.
12. When the reading is stable, accept the buffer value using the meter's automatic buffer recognition feature or manually enter the value of the pH buffer at its measured temperature.
13. The meter should display a 92 to 102 % slope or 54 to 60 mV per pH unit, depending on the pH meter. Refer to the meter user guide for details on how the meter displays the calibration information.

pH Electrode Measurements

Measurement Recommendations

- Check the electrode slope daily by performing at least a two buffer calibration. The slope should be 92 to 102%.
- Unless otherwise specified, only use the recommended filling solution in refillable pH electrodes. The *pH Electrode Summary Table section* shows the electrode filling solutions that are recommended for the Thermo Scientific pH electrodes.
- If the electrode is refillable, uncover the fill hole during measurements to ensure a uniform flow of filling solution. The filling solution level inside of the electrode must be at least one inch above the sample solution level.
- The sample solution level must be above the pH electrode reference junction when the electrode is immersed in the sample.
- Between measurements, rinse the electrode with distilled water and then with the next solution to be measured. To reduce the chance of error due to polarization, avoid rubbing or wiping the electrode bulb. Use a lint-free tissue and gently blot the bulb.
- Use the Orion Star A, DUAL STAR and VERSA STAR stirrer probe, Cat. No. 096019 or a magnetic stir plate and stir bar to stir all buffers and samples at a moderate, uniform rate. The stirrer probe can be used with Orion Star A, DUAL STAR and VERSA STAR benchtop meters.
- If using a magnetic stirrer, place a piece of insulating material, such as polystyrene foam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.
- If the electrode is refillable and the electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely and hold the reference junction under warm running water. Empty any water from the electrode and fill it with fresh filling solution. For a more thorough cleaning, refer to the *pH Electrode Cleaning Procedures section*.
- Flat surface electrodes may be used on any moist surface or in liquids.
- Handle the micro pH electrodes with care. Do not touch the pH bulb and stem against the bottom or walls of the sample containers.

Sample Requirements

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

Electrodes with a glass body may be used in Nonaqueous solutions and solutions that contain organic solvents. A minimum of 20% water must be present in the sample for the best measurement results. A benefit of the ROSS Ultra and ROSS electrodes is that the filling solution composition may be changed depending on the sample requirements. The ROSS electrode filling solution, Cat. No. 810007, is 3 M KCl. If there is a great deal of drift when using a ROSS Ultra or ROSS electrode in Nonaqueous solutions or solutions that contain organic solvents, fill the electrode with a mixture of methanol and water saturated with KCl. The ratio of methanol to water should be similar to the sample composition. For solutions that precipitate in the presence of chloride ions, fill the ROSS Ultra or ROSS electrode with 10% KNO_3, Cat. No. 900003.

The standard Ag/AgCl electrodes, micro Ag/AgCl electrodes and economy electrodes contain a single junction silver/silver chloride reference that will become clogged in solutions that contain silver complexing or binding agents such as TRIS buffer, proteins and sulfides. Frequent cleaning may be required when measuring these solutions, which will shorten the electrode life. To better measure pH in these solutions, use the ROSS Ultra electrodes, ROSS electrodes, AquaPro electrodes or double junction electrodes. Proteins cause the additional problem of coating the pH-sensing bulb, so extra care should be taken to keep the electrode clean while measuring samples that contain proteins. Regular use of the Orion pH electrode cleaning solution A for removal of proteins is recommended. See page 26 for details.

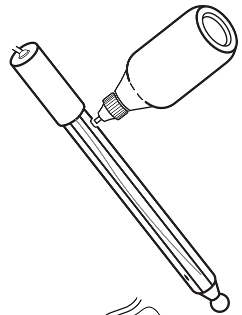
pH Measurement Procedure

1. Verify that the pH electrode was prepared and calibrated correctly. If the electrode is refillable, make sure that the fill hole is uncovered and the filling solution level is at least one inch above the sample solution level.
2. Rinse the electrode with distilled water and blot it dry with a lint-free tissue.
3. Place the electrode into the sample. Use the Thermo Scientific stirrer probe or a magnetic stir plate and clean stir bar to stir the sample at a moderate, uniform rate.
4. When the measurement is stable, record the pH value and temperature of the sample.

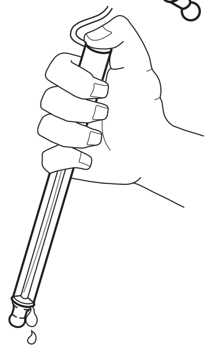
pH Electrode Maintenance

1. On a weekly basis, inspect the pH electrode for scratches, cracks, salt crystal build-up, or membrane/junction deposits.
2. Rinse off any salt build-up with distilled water. Remove any membrane/junction deposits by soaking the electrode in a 0.1 M HCl or 0.1 M HNO_3 solution for 15 minutes or soaking the electrode in a 0.1 M KCl solution heated to 55 °C for 15 minutes. If the electrode is dirty, clogged or coated, refer to the pH Electrode Cleaning Procedures section for a more thorough electrode cleaning procedure.
3. If a refillable electrode is used, drain the reference chamber, flush it with distilled water until all of the salt crystal build-up inside of the electrode is removed, flush it with fresh filling solution and fill the reference chamber with fresh filling solution.
4. Soak the electrode in ROSS pH electrode storage solution, Cat. No. 810001, or standard pH electrode storage solution, Cat. No. 910001, for 1 to 2 hours. The ROSS pH electrode storage solution is recommended for enhanced electrode performance.

Filling and Draining a Refillable pH Electrode



To fill an electrode, install the flip spout cap onto the filling solution bottle and lift the flip spout to a vertical position. Insert the spout into the electrode fill hole and add filling solution up to the fill hole. If a Sure-Flow electrode is used, push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode and release the cap to reset the Sure-Flow junction. Push down and release the cap until the junction returns to its original position and add filling solution up to the fill hole.



To drain most electrodes, insert a lint-free tissue or plastic pipet into the fill hole and remove all of the filling solution. If a pipet is used, do not insert the pipet too far into the electrode and do not touch the inner glass tube with the pipet.

To drain a Sure-Flow pH electrode, make sure that the fill hole is uncovered, place a waste beaker under the electrode and push down on the electrode cap to remove all of the filling solution. The filling solution will flow out of the Sure-Flow junction, near the pH bulb.

pH Electrode Storage

To ensure a quick electrode response and unclogged electrode junction, the electrode should never be stored dry and the pH-sensing bulb and reference junction must not dry out. Always store the pH electrode in pH electrode storage solution.

Short Term Electrode Storage (up to one week)

Soak the electrode in ROSS pH electrode storage solution, Cat. No. 810001, or standard pH electrode storage solution, Cat. No. 910001. For enhanced electrode performance, use ROSS pH electrode storage solution. The Thermo Scientific swing arm electrode stand, Cat. No. 090043, is pictured on the right.

To minimize the chance of breakage, the micro pH electrodes should be attached to an electrode stand and suspended in a beaker that contains storage solution. The electrode should not touch the sides or bottom of the beaker.

Long Term Electrode Storage (more than one week)

If the electrode is refillable, fill the reference chamber up to the fill hole with the appropriate electrode filling solution and securely cover the fill hole with parafilm. Cover the pH-sensing bulb and reference junction with a protective cap, sleeve or storage bottle that contains storage solution. Before returning the electrode to use, prepare it as a new electrode.

Cat. No.	Description
910001	Standard pH electrode storage solution, 475 mL bottle
910060	Standard pH electrode storage solution, 5 x 60 mL bottles
810001	ROSS pH electrode storage solution, 475 mL bottle
910003	Storage bottles for electrodes with a 12 mm diameter, pack of 3
910004-WA	Storage bottles for electrodes with an 8 mm diameter, pack of 3 (semi-micro epoxy pH electrodes)
910006-WA	Storage bottles for electrodes with a 6 mm diameter, pack of 3 (semi-micro glass pH electrodes)
090043	Swing arm electrode stand
810017	The Thermo Scientific Orion Storage Sleeve and Base is for use with pH electrodes that are 120mm or less in length that have a diameter of 12mm. The sleeve protects your electrode from breakage when not in use and it won't tip over due to its weighted removable base. As an additional convenience, the pH bulb stays conditioned while in storage so that it's ready to use when removed from the sleeve.

pH Electrode Troubleshooting Guide

General Troubleshooting Procedures

Follow a systematic procedure to isolate the problem. The pH measuring system can be divided into four components: 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 pH meters include an instrument checkout procedure and BNC shorting cap for convenience in troubleshooting. Refer to the pH meter user guide for details.

Electrode

To test the electrode operation:

1. Connect the electrode to a working meter that has a mV measuring mode. Set the meter to the mV mode.
2. Rinse the electrode with distilled water, blot it dry with a lint-free tissue and insert the electrode into fresh pH 7 buffer. When the reading is stable, record the mV value of the pH 7 buffer. The mV value should be -30 to +30 mV.
3. Rinse the electrode with distilled water, blot it dry with a lint-free tissue and insert the electrode into fresh pH 4 buffer. When the reading is stable, record the mV value of the pH 4 buffer. The mV value should be +150 to +210 mV.
4. Calculate the absolute mV difference between the two buffers. The absolute 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, open new pH buffers and repeat the procedure, clean the electrode thoroughly as directed in the *pH Electrode Cleaning Procedures section* and soak the pH electrode overnight in storage solution. If the electrode is refillable and the electrode response is slow or drifting, drain and refill the electrode with fresh filling solution. Replace the electrode if cleaning and maintenance fail to rejuvenate it.

Sample/Application

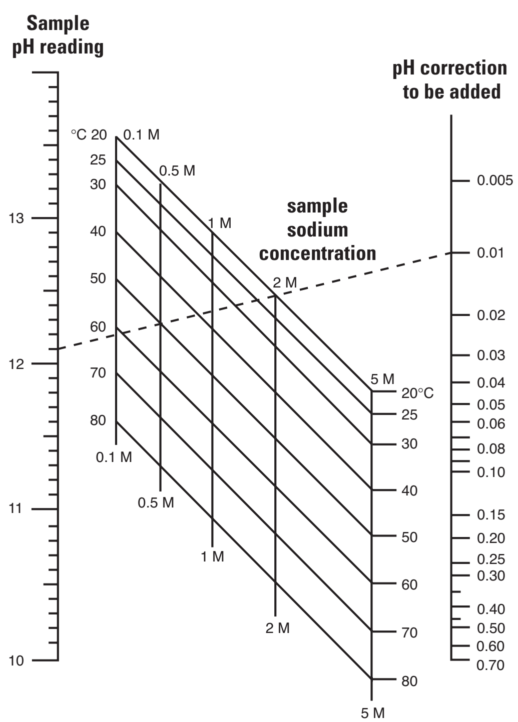
The electrode may work properly with pH buffers, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects.

Technique

If trouble persists, review operating procedures. Review the *pH Electrode Calibration section* and *pH Electrode Measurements section* to be sure proper technique has been followed.

pH Electrode 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.



Sodium Error Example

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

pH Electrode Cleaning Procedures

One of the most common reasons for a pH electrode to not work properly is because it is dirty, clogged or coated with sample. Cleaning a dirty, clogged or coated electrode restores proper electrode performance and prolongs the useful life of the electrode.

The Thermo Scientific pH electrode cleaning solutions are designed to simplify pH electrode maintenance and the ready-to-use cleaning solutions include a small beaker to hold the cleaning solution and a plastic pipet for removing the electrode filling solution. The cleaning solution kit, Cat. No. 900020, features one bottle of each cleaning solution for operators who are working with a variety of sample matrices.

Optimal cleaning procedures are dependent upon the sample type, extent of build-up or clogging and the type of electrode. The following instructions provide a starting point for developing an effective cleaning procedure.

1. Choose a cleaning solution. Cleaning solution D is a mild cleaning solution and cleaning solution C is a stronger cleaning solution. Cleaning solution A is for removing protein deposits and cleaning solution B is for removing bacterial contaminants.

2. Shake the cleaning solution. Pour enough of the cleaning solution into the beaker to cover the electrode junction. Refer to Figure 1 on page 6 for the location of typical pH electrode components, such as the electrode junction.

3. Soak the electrode for five to ten minutes in the cleaning solution while moderately stirring the solution. Electrodes with wick junctions may require more cleaning time.

4. Remove the electrode from the cleaning solution and rinse it thoroughly with distilled water to remove all traces of the cleaning solution.

5. If cleaning a refillable electrode, remove the filling solution from the electrode using the pipet that is included with the kit and add fresh filling solution to the electrode. Repeat this step two or three times for optimal electrode performance.

6. If cleaning a Sure-Flow electrode, flush a few drops of filling solution through the electrode junction by pressing down on the electrode cap. Ensure that the junction flushes and resets properly. Refill the electrode with filling solution.

7. Soak the electrode in ROSS pH electrode storage solution, Cat. No. 810001, or standard pH electrode storage solution, Cat. No. 910001, for at least 30 minutes.

8. Rinse the electrode thoroughly with distilled water and measure samples as usual. If the electrode response is slow or the electrode does not calibrate correctly, repeat the cleaning procedure. Viscous samples and samples that contain solid materials often require additional cleaning and additional filling solution changes.

Cat. No.	Description
900020	pH electrode cleaning solution kit, 1 x 30 mL bottle each of cleaning solution A and C, 1 x 60 mL bottle each of cleaning solution B and D, beaker and pipet
900021-WA	pH electrode cleaning solution A, removes protein contaminants, 4 x 30 mL bottles, beaker and pipet
900022-WA	pH electrode cleaning solution B, removes bacterial contaminants, 4 x 60 mL bottles, beaker and pipet
900023	pH electrode cleaning solution C, for general cleaning, 4 x 30 mL bottles, beaker and pipet
900024	pH electrode cleaning solution D, removes oil and grease contaminants, 4 x 60 mL bottles, beaker and pipet

Role of Solution Quality in pH measurement

Using high-quality solutions to calibrate and maintain your sensors is the best way to ensure your data is both accurate and reproducible. Avoid using low-quality, home-made, or expired buffers. These can lead to measurement errors, which require lengthy troubleshooting, or may go unnoticed. When choosing or making your own buffers and solutions for pH measurement, pay attention to the quality of the water and chemicals used. Use USP grade water whenever possible. Orion solutions are made with USP-grade purified water and are traceable to NIST certified standards. They undergo rigorous quality testing throughout the process to prevent contamination before and after bottling. To see a full list of Orion Solutions visit: http://www.thermoscientific.com/orionsolutions

Recommended Shelf Life for Buffers and Solutions

Unopened Thermo Scientific pH buffers and electrode filling solutions are NIST traceable. All buffers, except for pH 10.1, have an expiration date of two years from the date of manufacturing. pH 10.1 buffer has an expiration date of 18 months from date of manufacture. Certificates of analysis, which include the expiration date, are available online. Visit www.thermoscientific.com/waterCoA and enter the product catalog number (i.e. 910107) and lot code into the search box. The search results will include a link to the certificates of analysis for the product. The lot code is printed on the bottom or side the solution bottle and consists of two letters followed by a number (i.e. LQ1).

Once a pH buffer or electrode filling solution is opened, discard the unused portion after 2 to 3 months. Once pH 10.01 buffer is opened, discard the unused portion after 1 month, since pH 10.01 buffer is vulnerable to carbon dioxide contamination. Never pour used pH buffers or electrode filling solutions back into the bottle.

Common pH Sample Issues and Remedies

pH Measurements in TRIS Buffer, Protein and Sulfide Samples

TRIS [tris (hydroxymethyl) aminomethane] is a compound frequently used as a biological buffer, sulfide is common in wastewater and petroleum products and proteins are often in food products, wastewater and biological samples. When a single junction Ag/AgCl pH electrode is used in TRIS buffer, protein or sulfide samples, the sample will complex with the silver in the electrode and clog the electrode junction, preventing stable pH measurements. Proteins also coat the pH-sensing bulb. For the most accurate results and most stable measurements in these samples, use a pH electrode with a ROSS or double junction Ag/AgCl reference. The ROSS Ultra, ROSS, AquaPro and Double Junction pH electrodes are recommended for measuring the pH in TRIS buffer, protein or sulfide samples. When measuring protein samples, soak the pH electrode in ROSS pH electrode storage solution, Cat. No. 810001, between measurements to remove the protein coating. When cleaning the electrode is required, use Orion pH electrode cleaning solution A, Cat No. 900021-WA, for protein removal.

pH Measurements in Solid Samples and Surface pH Measurements

Solid and semi-solid samples include cheese, meat, powders, paper and agar gels. There are many methods available for measuring the pH of solid and semi-solid samples that include using a flat surface pH electrode, using a spear tip pH electrode, and mixing or blending a fixed amount of sample with distilled water. Once a method is established that is compatible with the sample, the method should be followed exactly with all samples for the most reproducible measurements.

If the sample is soft or semi-solid, use a spear tip pH electrode and pierce the sample with the electrode to a fixed depth. If the surface of the sample is moist, use a flat surface pH electrode and measure the surface of the sample. The sample must be moist enough for the pH-sensing bulb and the reference junction to make adequate contact with the sample. If necessary, add a drop of distilled water or potassium chloride to wet the surface before placing the electrode on the sample. For the best reproducibility, all samples should have the same amount of liquid added before measurement.

If the sample is soluble in water or disperses readily in water, mix a fixed percent of sample with a fixed quantity of water and measure the resulting solution. Up to 25 % sample by weight or volume is commonly used. Since each sample is different, the details of the method should be determined through trial and error with the sample. For cheese samples – blend 5 grams of cheese with 100 mL of distilled water and stir the solution thoroughly, stop stirring and wait 5 minutes to let the solids settle and then measure the pH of the liquid portion. For paper samples – soak 1 gram of paper pieces in distilled water, wait 10 minutes and measure the pH of the liquid. For soil samples – mix a fixed ratio of soil and distilled water and stir the solution thoroughly, stop stirring and wait a fixed amount of time to let the solids settle and then immerse the pH electrode at a fixed depth and measure the pH of the liquid portion.

pH Measurements in Pure Water Samples

Pure water samples include distilled water, deionized water, some process waters, well water, some surface waters, treated effluent, boiler feed water and rain water. In pure water samples the pH electrode response tends to drift and is slow, non-reproducible and inaccurate. Measurements in these samples are more difficult because of the low conductivity of the sample, differences between the low ionic strength solutions and normal ionic strength buffers, changes in the liquid junction potential and the absorption of carbon dioxide into the sample. Since pure water solutions have a low conductivity, the solution will tend to act as an antenna and the electrode response can be noisy.

Calibration of a pH electrode in high ionic strength buffers will increase the time required for stabilization when measuring a low ionic strength sample. In addition, the possibility of sample contamination will be increased. For most precise measurements, buffers and samples should have a similar ionic strength. When two solutions come in contact, diffusion occurs until an equilibrium is reached. Since ions have different mobility and diffuse at different rates, a charge imbalance occurs at the point of contact. A liquid junction potential occurs when the electrode filling solution meets the sample. This charge imbalance will be large if there is a large difference in composition between the filling solution and the sample. It is important that the junction potential be constant during measurement. If the two solutions are quite different, normal fluctuations in the boundary layer will produce noise. Constant, reproducible junction potentials are achieved by measuring samples and standards with similar ionic strengths. Since pure waters contain little dissolved material, their buffering capacity is small. Absorption of carbon dioxide from the atmosphere will cause a slow change in pH, observed as a drifting pH reading and a different pH from the original sample. Samples that are not previously saturated with carbon dioxide must be handled with care.

The Thermo Scientific™ Pure Water™ pH test kit, Cat. No. 700001, has been developed to minimize the problems encountered when measuring pH in pure waters. This test kit uses a pure water pH additive called pHISA™ adjustor and low ionic strength buffers that contain the same background as the pHISA adjustor. For the most accurate results, a ROSS Ultra or ROSS pH electrode is recommended. Adding pHISA adjustor to samples increases the ionic strength, reducing the noise and improving the response time. The shift in pH caused by the addition of pHISA adjustor is minimal – between 0.005 and 0.01 pH units. Since the same amount of pHISA adjustor is added to the buffers and samples, the net effect on the pH is negligible. Calibration is performed using the low ionic strength buffers with pHISA adjustor already added. Measuring with samples and buffers with the same ionic strength increases accuracy, precision and time response. Contamination due to carryover from higher ionic strength buffers is also minimized.

pH Measurements in Sludges, Suspensions, Colloids, Slurries and Viscous Samples

Sludge, suspension, colloid, slurry and viscous samples include wastewater, mud, paper pulp and corn syrup. These samples clog the electrode junction and coat the pH-sensing bulb, resulting in slow electrode response, measurement drift and pH measurement errors. The thickness of the sample can also cause a sample carryover problem – after the pH electrode is removed from the sample, some of the sample may cling to the electrode.

For the most accurate results and most stable measurements in these samples, use a pH electrode with a Sure-Flow or open junction and soak the pH electrode in ROSS pH electrode storage solution, Cat. No. 810001, between measurements. For the best reproducibility, immerse the pH electrode at a fixed depth in all samples. Sure-Flow junctions resist clogging, provide a constant flow of filling solution and are extremely easy to clean. Open junctions resist clogging, contain a low maintenance polymer gel as the filling solution and are easy to clean. The ROSS Sure-Flow, Ag/AgCl Sure-Flow and AquaPro pH electrodes are recommended for measuring the pH in sludge, suspension, colloid, slurry and viscous samples. The ROSS pH electrode storage solution will enhance the pH electrode performance by acting as a very mild cleaning solution. For a more thorough cleaning procedure, refer to the *pH Electrode Cleaning Procedures* section.

pH Measurements in Extreme pH or High Salt Content Samples

Samples with a pH less than 2, pH greater than 12 and salt content greater than 0.1 M include battery acid, copper plating solutions and brines. These samples create measurement issues with the reference portion of the pH electrode, due to the liquid junction potential. The liquid junction potential occurs when there is a large difference in composition between the filling solution and the sample, resulting in measurement drift and slow electrode response.

In samples with a pH of 2 to 12 or salt content less than 0.1 M, the liquid junction potential is rarely a problem since the filling solution is formulated for the best performance under these conditions. In samples with a pH less than 2, pH greater than 12 or a salt content greater than 0.1 M, a pH electrode with a ROSS or double junction Ag/AgCl reference is recommended. The filling solution of the ROSS Ultra, ROSS and refillable Double Junction pH electrodes can be modified to match the sample composition, which will reduce the liquid junction potential and provide accurate, more stable measurements in these samples.

For samples with a pH greater than 12, add a dilute base to the recommended electrode filling solution to raise the filling solution pH. For samples with a pH less than 2, add a dilute acid to the recommended electrode filling solution to lower the filling solution pH. For samples with a high salt content, use a strong solution of the same salt as the electrode filling solution. For example, when measuring the pH of sodium bromide brines, use sodium bromide in the outer chamber of a double junction electrode.

pH Measurements in Nonaqueous Samples

Nonaqueous samples contain liquids other than water and include oils, alcohols, cosmetics, methanol and acetone. These samples produce unstable readings, slow electrode response and pH measurement errors due to high sample resistance, bulb dehydration, sample carryover contamination and liquid junction potentials. The high resistance (low conductivity) of many organic solvents causes noise and slow electrode response. To avoid this, an electrode with a low resistance glass bulb should be used. It is often helpful to add a small amount of an inert salt (for example, a quaternary ammonium salt) to increase the conductance of the solution. Addition of a salt will change the activity of the hydrogen ion, causing a small shift in the pH; however, the error is small when compared with measurement drift issues.

Slow electrode response and drift are also caused by the dehydration of the glass pH sensing bulb. For the pH sensing bulb to function, the surface of the glass must be hydrated so hydrogen ions can be absorbed onto the surface of the glass. A nonaqueous solution causes the dehydration of the pH sensing bulb and frequently soaking the pH electrode in water or a pH buffer hydrates the bulb, providing a faster, more stable response. To prevent contamination of samples due to carryover on the electrode bulb, the electrode should be rinsed between measurements with a solvent that will dissolve the sample material from the electrode, and then rinsed with a volatile solvent like acetone to remove the rinse solution, followed by soaking it in a pH buffer.

Large liquid junction potentials that cause unstable readings are a problem when measuring nonaqueous samples. When a reference electrode with an aqueous filling solution comes in contact with a nonaqueous sample, unequal diffusion of ions occur, causing continuous measurement drift. To minimize this problem, the electrode filling solution should be modified to provide compatibility with the sample and minimize junction potential problems. A refillable electrode with a double junction reference, such as a ROSS Ultra or ROSS pH electrode, should be used to allow the filling solution to be easily modified. Several alternative filling solutions can be used and include a mixture of methanol and water saturated with KCl, glacial acetic acid saturated with KI, acetone saturated with KI and methanol saturated with LiCl. When using a solvent in the filling solution, a salt must be added to improve the electrical conductance. KI is often more soluble than KCl and can be substituted as required. When adjusting the filling solution, allow the electrode to reach equilibrium overnight before using it. Solvent-based filling solutions should not be used in epoxy body electrodes. Since epoxy body electrodes should not be used in certain solvents, especially highly polar organic solvents, a glass pH electrode should be used.

The pH value of a nonaqueous solution cannot be accurately compared to an aqueous buffer. The activity of the hydrogen ion varies, depending on the background medium, due to the differences in dielectric constants, solvent acidities and ion mobilities. The pH values obtained when measuring nonaqueous samples can only be used as relative measurements, to compare the acid-base qualities of similar solvents or to indicate when adjustments in pH are needed. The readings cannot be reported as actual pH values, since the pH scale is based on the relative acidity or alkalinity of water.

Resources for Electrochemistry and Water Analysis Equipment

Thermo Scientific Orion Products

Visit www.thermoscientific.com/water for additional information on laboratory and field equipment for pH, ISE, conductivity and dissolved oxygen analysis and spectrophotometry, colorimetry and turbidity products.

Water Analysis Instruments Online Library

Visit www.thermoscientific.com/WAI-Library to access product literature, user guides and manuals, software updates and additional support files. For the most up-to-date MSDS and C of A files for Thermo Scientific Orion solutions, visit www.thermoscientific.com/waterMSDS.

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