How electrode design correlates with optimum performance in pH measurement

Abstract

This white paper explores how unique design features and iodide/triiodide ion pair reference chemistry help Thermo Scientific™ Orion™ ROSS™ pH electrodes deliver fast, stable, and accurate measurements.

When pH measurement performance counts

A pH measurement, along with temperature and weight, is one of the most common measurements performed in laboratories. Reliable and accurate pH measurement is critical for ensuring the quality and safety of drinking water, as well as most pharmaceutical, personal care, and food products. Many industrial processes, such as chemical production, petrochemical production, and wastewater treatment, require constant pH monitoring to help control the process and ensure a quality product.

Reliable and accurate pH measurement is highly dependent upon both the design and manufactured quality of the pH electrode. Of all the electrode features that influence the performance of pH probes, the reference element and the composition of the sensing glass are the most critical. The ideal pH probe incorporates highly conductive sensing glass that is sensitive to H^+ ions and insensitive to interfering ions like Na^+. It also has a highly efficient and stable internal reference system that is minimally affected by changes in temperature. These features contribute to a fast, accurate pH response in a variety of sample measurements under many different conditions. Electrodes should also be designed to deliver stability and a long product life with minimal maintenance. Regardless of the nature and temperature of the sample, an ideal electrode is designed to provide results that are accurate, fast, stable, and reproducible.

Limitations of conventional electrodes based on metal/metal salt reference systems

Standard pH electrodes utilize heterogeneous reference chemistry, typically silver in contact with a saturated solution of sparingly soluble silver chloride and a fixed level of chloride ions. Since the solubility of silver chloride has a large temperature coefficient, meaning that small temperature changes cause large changes in silver chloride solubility, silver/silver chloride reference chemistry imposes inherent limitations on these electrodes. As a consequence of slow solid–liquid equilibrium in response to temperature changes within the reference system, pH probes that use this reference chemistry can exhibit poor accuracy, slow response, and response drift.

Although temperature compensation can be applied to electrodes containing conventional metal/metal salt reference systems, these electrodes often do not conform to assumptions that are necessary to apply compensation. The ideal response of a pH electrode (in mV) is governed by the Nernst equation, which predicts how the signal will be affected by temperature when equilibrium is achieved. An example of electrode signal response at various temperatures is shown in Figure 1.

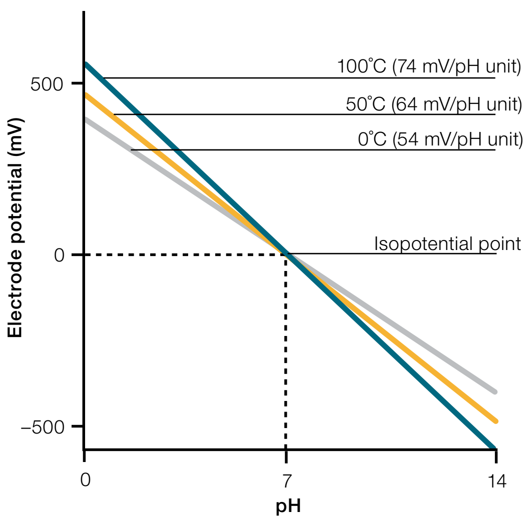

Figure 1. Change in Nerstian slope of an electrode with temperature.

By symmetrical design, all the mV/pH response curves at various temperatures can intersect at a single point, known as the isopotential point, which is usually near pH 7. At this point, the mV signal is not affected by temperature.

When equilibrium is reached, temperature compensation can be executed accurately based on the model built on the curves. However, since a conventional metal/metal salt reference electrode is slow to reach equilibrium, the accuracy of temperature compensation applied for the measurement is adversely affected.

Since the solubility of silver chloride is proportional to temperature in this system, more silver chloride can dissolve from the coated wire as the temperature increases. However, the silver chloride does not re-deposit on the wire when the temperature decreases again. So what happens to the silver chloride particulates? They can fall to the bottom of the reference portion of the electrode or precipitate in the junction, where the electrolyte contacts the sample. This can clog the junction, which can cause electrode performance to deteriorate very rapidly.

The silver/silver chloride reference system has also been found to contribute to the contamination of certain types of samples, such as proteins [1,2]. This occurs through complexation of silver ions with the sample or sample matrix. Many electrodes that employ the silver/silver chloride reference system require complex engineering in order to mitigate these inherent issues.

Benefits of an iodide/triiodide ion pairing reference system

Unlike silver/silver chloride–based pH probes, ROSS pH electrodes have a reference system that incorporates homogeneous iodide/triiodide chemistry [3]. Iodide/triiodide ions are completely soluble over a wide range of temperatures, and the ion pairing system quickly attains equilibrium without hysteresis due to slow solid–liquid equilibrium. The formulation used for the ROSS reference system results in a minimal temperature coefficient, so ROSS pH electrodes offer great stability and rapid response, even in situations where the temperature at the point of measurement varies widely. In addition, the iodide/triiodide reference system does not produce any precipitate, which can contribute to clogging of the junctions or sample contamination. The electrolyte in ROSS electrodes is designed to be stable and equitransferent, resulting in a low junction potential and rapid potential stabilization. This enables the electrodes to deliver results quickly without frequent recalibration.

The iodide/triiodide reference system in ROSS electrodes is designed to deliver outstanding accuracy, response time, stability, and reproducibility in pH measurements, regardless of the temperature at the point of testing. ROSS electrode specifications include:

- Stabilization to 0.01 pH units in less than 30 seconds when checking samples using pH 6.86 buffer that vary in temperature by 50°C (25–75 °C)
- Measurement accuracy to ±0.03 pH units and precision to ±0.01 pH units using the same buffer and automatic temperature compensation

Electrode performance enhancements due to the coil design of the reference cell in ROSS electrodes

One of the challenges in electrode design is balancing the performance needs of the user with design constraints related to the chemical and physical properties of the materials in the electrode. A major advantage of temperature-insensitive ROSS reference chemistry is that it eliminates the need for the reference and sensing electrode wires to be located in physical symmetry with the sample. The ability to place the reference electrode wire far from the sensing electrode wire allows a design that protects the reference electrode.

This is where innovative design can dramatically improve electrode performance, as illustrated by one of the design features of the ROSS electrode reference system (Figure 2). The distinctive orange coil is highly visible in the glass body version of ROSS electrodes. It not only gives ROSS electrodes their distinctive look, but is also a feature designed to increase electrode lifetime [4]. Building a coil into the reference system provides the electrode with two advantages over a straight stem design. By significantly increasing the diffusion path to the reference wire, the coil minimizes changes near the reference wire caused by diffusion of the fill solution through the reference junction to the inner electrolyte. The effective diffusion path is further increased by incorporating particles or polymers into the inner fill solution. The amount of reference fill solution is also greater than that of a straight stem design.

Each of these features contribute to a reference system that lasts longer. When combined, they result in a long-lasting electrode. The addition of a reference fill solution reservoir to the caps of Thermo Scientific™ Orion™ ROSS Ultra™ electrodes enables them to have long warranties. Refillable models are covered for two years, and low-maintenance gel-filled models are covered for 18 months [5].

Figure 2. Distinctive orange coil design of the Orion ROSS electrode reference system.

Advantages of the double junction probe design of Orion ROSS electrodes

Many metal/metal salt reference–based pH electrodes available today have a double junction design, primarily to protect samples from metal salts generated by the reference system. Since there are no metal salts in the ROSS reference system, the double junction electrode design serves two purposes. First, the ROSS double junction isolates and protects the reference from the sample to help maintain a stable, accurate, drift-free reference potential. Second, the double junction probe design gives the user the ability to adapt the outer fill solution for optimal compatibility with their sample type. This is useful when regular potassium chloride outer fill solution contains ions that interfere or react with the sample, such as when the sample has low ionic strength or is nonaqueous. This is often the case with pharmaceutical samples and petrochemical titration applications.

Helping make complex measurements routine, reliable, and accurate since 1962

When John Riseman, who developed a dual-input pH meter, George Eisenman, Martin S. Frant, and Dr. James W. Ross met in the MIT Industrial Liaison Program in 1961, they made significant progress in optimizing pH electrodes and ion-selective electrodes (ISEs). Working with Corning Glass, they developed the first sodium ISE and the first sulfide ISE. They also developed the first “all-purpose” pH probe, which utilized low-resistance glass and covered the full pH range with low sodium error [6]. Today, Thermo Fisher Scientific is proud to carry on their tradition reflected in the ROSS pH electrode line of sensing technology.

Available sizes and styles of ROSS pH electrodes and ISEs

Because there are many different kinds of samples and measuring environments, ROSS electrodes have many different designs. ROSS pH electrodes and ISEs come in a wide variety of sizes and styles to serve a range of liquid sensing applications.

- Available with an epoxy body designed for impact resistance and durability or a glass body designed to resist corrosive materials and solvents (Figure 3)
- Choice of refillable and gel-filled models; constructed with junctions suited to a wide variety of samples, including the patented [7] Thermo Scientific™ Orion™ ROSS™ Sure-Flow™ annular sleeve junction (Figure 4), standard ceramic, glass fiber, and innovative glass capillary
- Thermo Scientific™ Orion™ Triode™ pH/ATC electrodes with built-in temperature sensors for automatic temperature compensation available; designed to conveniently deliver accurate pH measurements over a wide range of temperatures
- Manufactured with a variety of bulb shapes for many applications, including standard, semi-micro, micro, rugged bulb, spear tip, and flat surface tip (Figure 5)
- Fitted with standard BNC connectors that are compatible with Thermo Scientific™ meters and other current brands of meters; many available with fittings for titrators

Conclusion

Whether you are working on your next great innovation, diligently testing your products to ensure quality, optimizing a manufacturing process, or performing critical testing for others, pH probes are important instruments in your laboratory or test kit. The unique reference chemistry of ROSS electrodes is designed to deliver outstanding accuracy and trouble-free measurements, making ROSS electrodes an ideal choice for pH measurement when performance counts.

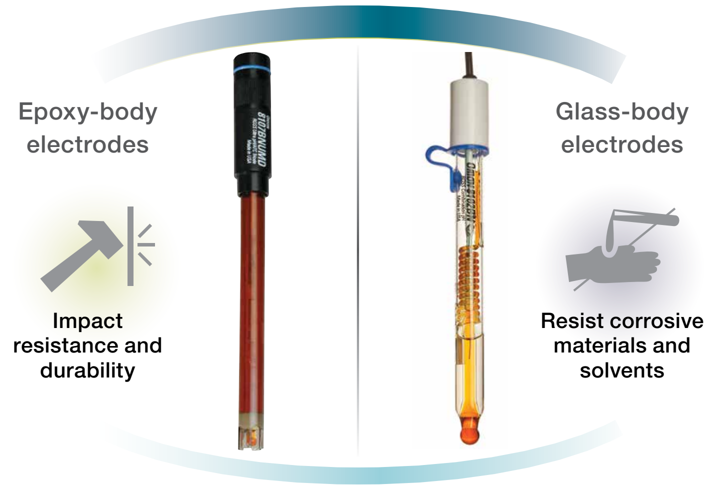

Figure 3. Design options for various ROSS pH electrodes.

Figure 4. Orion ROSS Sure-Flow junctions resist clogging, provide a constant flow of filling solution, and are extremely easy to clean.

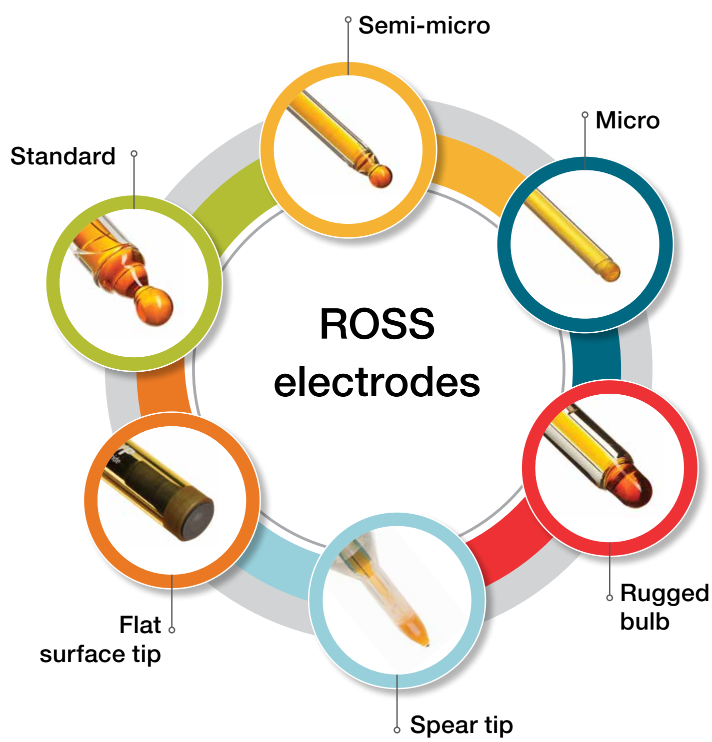

Figure 5. Bulb shapes designed for a wide variety of applications.

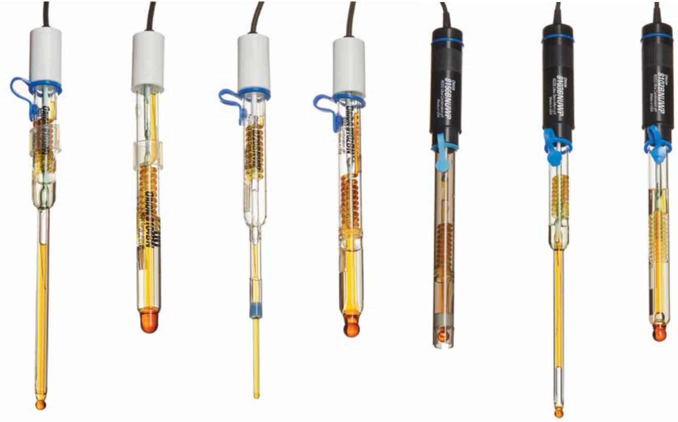

Table 1. pH electrode recommendations by sample type.

Sample or application	We suggest
Biological and pharmaceutical—Tris buffer, proteins, enzymes	Electrode with a ROSS or double junction Ag/AgCl reference (no sample contact with silver)
Education, student use	Epoxy-body electrode for durability
Emulsions—foods, cosmetics, oils	Electrode with a Sure-Flow or open junction to prevent clogging
Emulsions—petroleum products, paint	Glass-body electrode that resists damage from samples and a Sure-Flow or open junction to prevent clogging
Flat surfaces—cheese, meat, agar	Electrode with a flat surface tip and a ROSS or double junction Ag/AgCl reference (no sample contact with silver)
Flat surfaces—paper	Electrode with a flat surface tip
General purpose—most sample types	Most electrodes can be used for general purpose measurements. We recommend an electrode containing a ROSS reference system for measurements that require fast response, high precision (± 0.01 pH units), or high stability.
Harsh environments—field or plant use, rugged use	Epoxy-body electrode for durability and polymer or gel-filled for easy maintenance
High ionic strength—acids, bases, brines; pH > 12 or pH < 2	Electrode with a Sure-Flow or open junction for better contact with samples and more stability
High temperatures	Electrode with a ROSS reference for longer life and/or a quick flow junction for fast response
Hydrofluoric acid (HF) samples	Electrode with a rugged or durable glass bulb and a double junction to protect the reference
Large sample—tall flask	Electrode with a long body that fits the container
Low ionic strength—treated effluent, deionized water, distilled water	Refillable pH probe for better contact with samples and more stable measurements
Nonaqueous—solvents, alcohols	Glass-body electrode that resists damage from samples and a Sure-Flow junction for better sample contact and stability
Semi-solids—fruit, meat, cheese	Electrode with a spear tip for piercing samples and a ROSS or double junction Ag/AgCl reference
Small sample—microtiter plate	Electrode with a small diameter to fit inside the container (micro electrodes are a good choice for this application)
Small sample—NMR tube	Electrode with the right diameter and body length to fit inside the container
Small samples—test tube, small flask, beaker	Electrode with a small diameter to fit inside the container: • Semi-micro electrodes are suitable for most samples with volumes down to 200 µL. • Micro electrodes are designed to measure small volumes down to 0.5 µL. They are very delicate and should be handled with care.
Small samples—Tris buffer, proteins, sulfides	Electrode with a small diameter to fit inside the container and a ROSS reference
Titration	Electrode with a Sure-Flow or sleeve junction for better sample contact and stability
Viscous liquids—slurries, suspended solids, sludges	Electrode with a Sure-Flow or open junction to prevent clogging
Water—acid rain, boiler feed water, distilled water, rain water, well water	Electrode with a ROSS or double junction Ag/AgCl reference and refillable pH probe design for better sample contact
Water—drinking water, tap water	Epoxy-body electrode for durability
Water—wastewater, seawater	Electrode with a ROSS or double junction Ag/AgCl reference and an epoxy body for durability

References

1. Klueh U, Wagner V, Kelly S et al. (2000) Efficacy of silver-coated fabric to prevent bacterial colonization and subsequent device-based biofilm formation. *J Biomed Mater Res* 53(6)621–631.
2. Yamanaka M, Hara K, Kudo J (2005) Bactericidal actions of silver ion solution on *Escherichia coli*, studied by energy-filtering transmission electron microscopy and proteomic analysis. *Appl Environ Microbiol* 71(11):7589–7593.
3. US patent number 4,495,050. Title: Temperature insensitive potentiometric electrode system. Inventor: Ross JW (Cambridge, MA); family ID: 26906071; application number: 06/466,856; filed February 16, 1983.
4. Coil design trademark registration number: 3122603, August 1, 2006.
5. US patent number 6,793,787. Title: Ion-selective electrode. Inventors: Hirshberg M (Brookline, MA), West S (Hull, MA), Barbookles J (Ipswitch, MA); application number: 10/098,687; date: September 21, 2004.
6. Frant MS (1994) History of the early commercialization of ion-selective electrodes. *Analyst* 199:2293–2301.
7. European patent number WO 88/01739 (10.03.88 88/06). Inventor: Hirshberg M (Brookline, MA); application number: 87905992.1; filed August 25, 1987.

When pH measurement is critical

Find out more at **thermofisher.com/rossph**