White Paper

How Electrode Design Correlates with Optimum Performance in pH Measurement

Key Words

pH electrode, ROSS, ROSS Ultra, Triode, pH measurement, titration, iodide/triiode pairing, double-junction, temperature compensation, reference electrode, coiled reference system, ROSS reference system

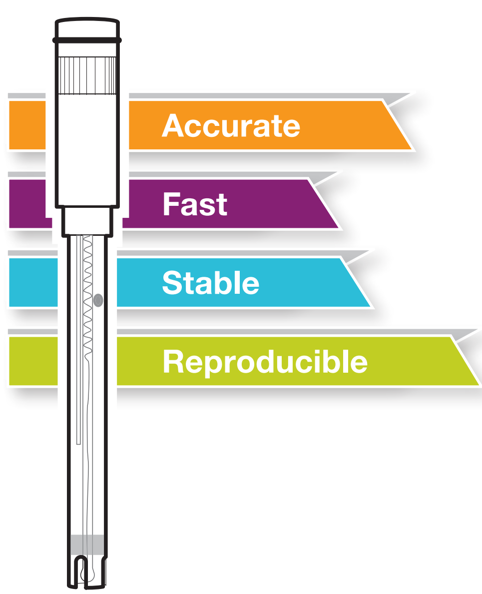
Abstract

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 three 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. Additionally, many industrial processes, such as chemical and 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 parts which influence the performance of pH electrodes, the reference element and the composition of the sensing glass are the most critical. The ideal pH electrode incorporates a highly-conductive sensing glass which is sensitive to H^+ ion and insensitive to interfering ions such as Na^+ and a highly efficient and stable internal reference system, which is minimally affected by changes in temperature. These features contribute to fast, accurate pH response in a variety of sample measurements in 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:



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Limitations of conventional electrodes based on metal/metal salt reference systems[3]

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 (small temperature changes cause large changes in silver chloride solubility), the silver/silver chloride reference chemistry imposes inherent limitations on these electrodes. As a consequence of the slow solid-liquid equilibrium in response to temperature changes within the reference system, pH electrodes which use this reference chemistry can exhibit poor accuracy, slow response and response drift.

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

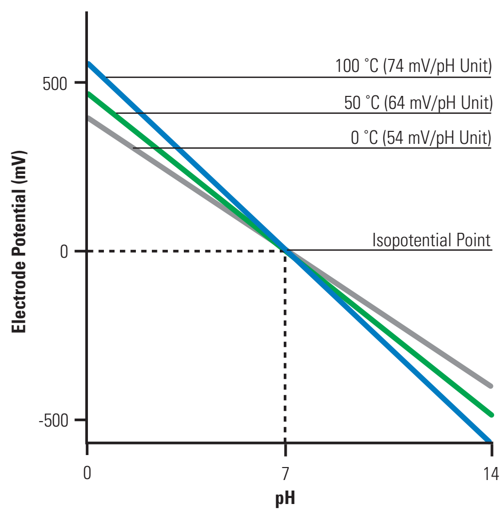


Figure 1: Change in Nerstian slope of an electrode with temperature

By symmetrical design, all the mV/pH response curves at various temperatures can intersect at a single point, known as the isopotential point, 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 upon the curves. However, since the conventional metal/metal salt reference electrode is slow to reach equilibrium, the accuracy of the temperature compensation used for the measurement is adversely affected.

In addition, since in this system the solubility of silver chloride is proportional to temperature, more silver chloride can dissolve from the coated wire as the temperature increases, but the silver chloride does not re-deposit on the wire when the temperature decreases again. So what happens to the particulates of sliver chloride? They can fall to the bottom of the reference part of the electrode or can 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 also has been found to contribute to contamination of certain types of samples, such as proteins[1][2], through complexation of the sliver ions with the sample or sample matrix. Many electrodes which employ silver/silver chloride reference system require complex engineering in order to mitigate these inherent issues.

Benefits of an iodide/triiodide ion pairing reference system[3]

Unlike sliver/sliver chloride based pH electrodes, ROSS pH electrodes have a reference system that incorporates an iodide/triiodide homogeneous chemistry. Iodide/triiodide ions are completely soluble over a wide range of temperatures and the ion pairing system quickly attains equilibrium without the hysteresis due to slow liquid-solid equilibrium. The formulation used in the ROSS reference system results in a minimal temperature coefficient, so ROSS pH electrodes offer great stability and fast 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 used in the ROSS electrode is designed to be stable and equitransferent, resulting in low junction potential and rapid potential stabilization. This enables the electrode to deliver fast results without frequent re-calibration.

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

- A stable response to 0.01 pH in less than 30 seconds when checking samples of pH of 6.86 buffer which vary in temperature by 50 °C (25-75 °C).
- Measurement accuracy to ±0.03 pH units and precision of ±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[4]

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 used in the electrode. A major advantage of the temperature insensitive ROSS reference chemistry is that it eliminates the need for the reference and sensing electrode wires to be located in physical symmetry to the sample. The ability to place the reference electrode far away from the sensing electrode provides the opportunity for a design which can protect the reference.
This is where innovation in design can dramatically improve electrode performance as illustrated by one of the design features of the ROSS electrode. The distinctive "orange coil", which is highly visible in the glass body version of the ROSS electrode, not only gives ROSS electrodes their distinctive look, but is a feature designed to increase electrode lifetime. Designing 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 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.

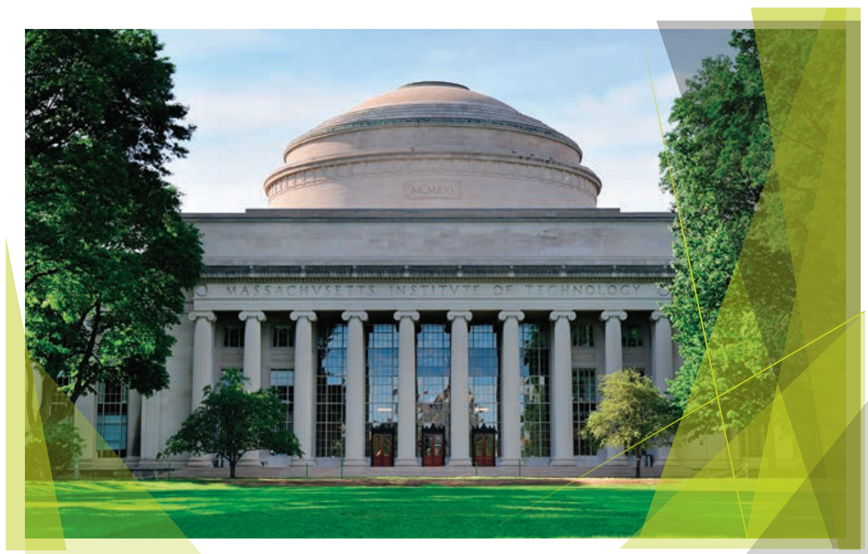
Distinctive "orange coil" design in the ROSS electrode

The amount of reference fill solution is also increased over a straight stem design. Each of these factors contributes to a longer lasting reference system; when combined, these features result in a longer lasting electrode. The addition of a reference fill solution reservoir to the cap of the Thermo Scientific™ Orion™ ROSS Ultra™ electrodes enables them to have a long warranty: two years for refillable models and 18 months for low-maintenance, gel-filled models[5].

Advantages of double junction design in ROSS electrodes

Many metal/metal salt reference-based pH electrodes available today have a double junction design, primarily to protect the sample from metal salts generated by the reference system. Since there are no metal salts in the ROSS reference, the double junction design of a ROSS electrode serves different purposes. First, the ROSS double junction isolates and protects the reference from the sample to help maintain a stable, accurate, drift-free reference potential. Secondly, the double junction design gives the user the opportunity to adapt the outer fill solution to be optimally compatible with their sample type. This is useful when the 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 non-aqueous, as often found in pharmaceutical samples or petrochemical titration applications.

Helping make complex measurements routine, reliable and accurate since 1962

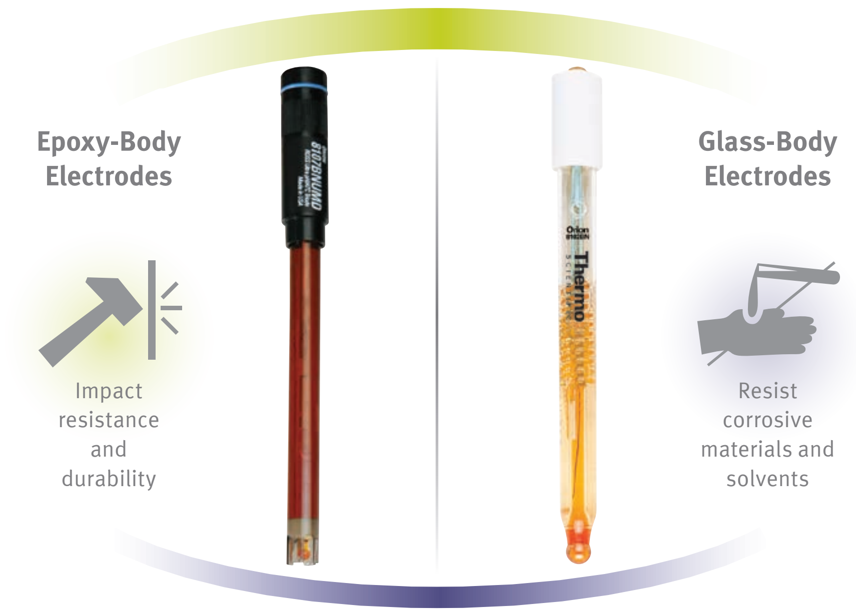


When John Riseman (who developed a dual-input pH meter), George Eisenman, Martin S. Frant and Dr. James W. Ross met at the MIT Industrial Liaison Program in 1961, they made significant progress in their work to optimize pH and ISE electrodes. Working with Corning Glass they developed the first sodium ion-selective electrodes (ISE), the first sulfide ISE and the first “all-purpose” pH electrode, 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.

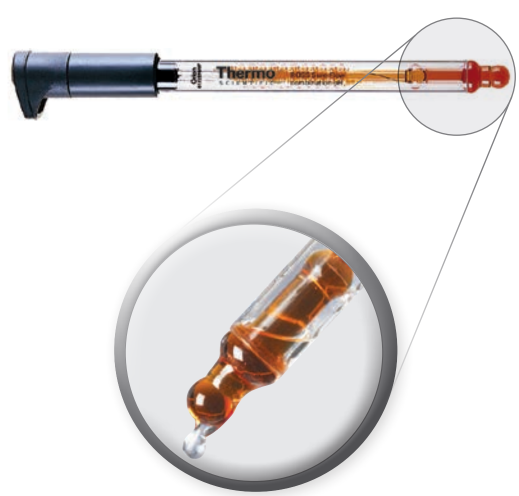
Available sizes and styles of ROSS pH and ISE electrodes

Because there are many different kinds of samples and many different measuring environments, ROSS electrodes come in many different designs. ROSS pH and ISE electrodes 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.

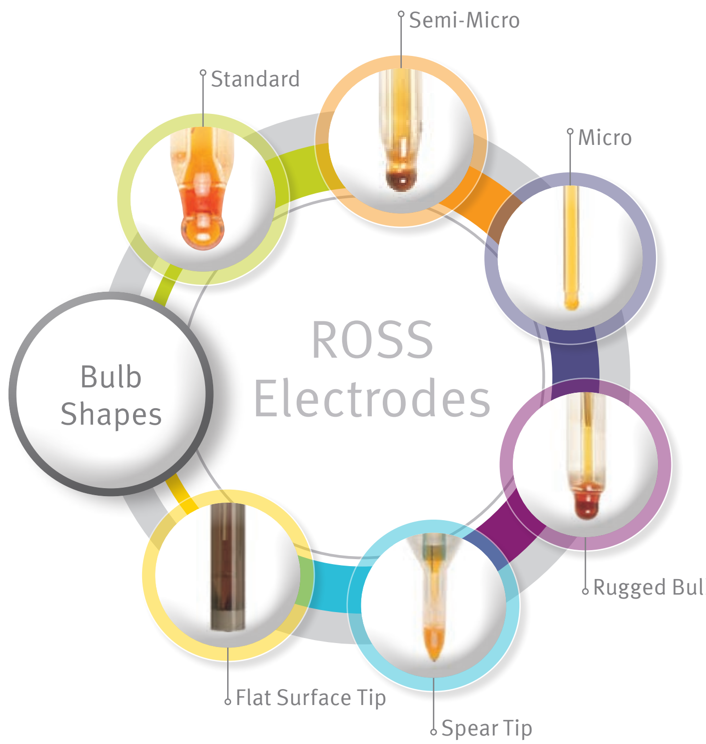


- Choice of refillable and gel-filled models. Constructed with junctions suited to a wide variety of samples, including the patented[7] Thermo Scientific™ Orion™ ROSS™ Sure-Flow™ annular sleeve junction, standard ceramic, glass fiber, and innovative glass capillary.



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

- Thermo Scientific™ Orion™ Triode™ pH/ATC electrodes with built-in temperature sensors for automatic temperature compensation are also available, designed to conveniently deliver accurate pH measurements along 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.



- Fitted with standard BNC connectors, which are compatible with Thermo Scientific and other current brands of meters and many are also 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 electrodes are an important instrument in your laboratory or test kit. The unique reference chemistry of ROSS electrodes are designed to deliver outstanding accuracy and trouble-free measurements, making ROSS electrodes an ideal choice for pH measurement when performance counts.

pH electrode recommendations by sample type

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

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