pH Electrode Selection Guide

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Use this guide to determine the electrode components and style that will work best for the solutions measured.

Electrode Components

Most pH electrodes are combination electrodes. An electrode comprises two main elements. One element is a sensing half-cell and the other is a reference half-cell. Both half-cell units must be used together to complete the pH circuit in order to get a pH measurement. The sensing half-cell is the portion of the electrode that is responsible for the measurement portion in the system; think of this as the positive ( ) end of the circuit. This portion of the electrode typically contains a membrane that is sensitive to the change in the pH of the solution being measured. The reference half-cell provides a stable reference potential that is needed for pH measurement; think of this as the negative (-) end of the circuit.

Most of the pH electrodes that Cole-Parmer offers are combination electrodes. Combination electrodes contain both half cells—the sensing and reference half-cell—in one single probe. Cole-Parmer also offers the traditional sensing and reference half-cells but they have become much less popular. The best option will depend on the type of samples that the user will measure. The following sections describe the different types of electrodes and explain key differences for each.

Epoxy vs Glass

Epoxy body electrodes are more durable, tend to be the more economical choice, and are ideal for environments where rough handling is expected. However, the maximum temperature limit for most epoxy body electrodes is approximately 176°F (80°C).

Glass body electrodes are capable of withstanding much higher temperatures, up to 230°F (100 to 110°C) depending on the specific electrode, and also offer chemical resistance to highly corrosive materials or solvents. Glass body electrodes are also easier to clean after use. Either electrode type will require care when handling, as even a small fracture to the bulb or body of the electrode can lead to erroneous readings.

ISFET Probes

Solid-state ISFET (ion-specific field effect transistor) electrodes with a non-glass measuring surface won't break and wipe clean for dry storage. This is a good choice for use in the food industry to avoid any chance of glass breaking and

contaminating samples. Another benefit of ISFET electrodes is their ability to measure smaller volumes of samples, in most cases as little as 30 microliters.

Sealed vs Refillable Electrodes

Sealed or gel-filled electrodes are virtually maintenance free and ideal for most applications. They also tend to be a more economical choice. However, once the inner fill solution level is low (or if it dries out), the electrode will have to be replaced. This is why sealed electrodes may have a shorter life span than a refillable electrode.

Refillable electrodes have a port near the top of the electrode which allows them to be refilled once the inner fill solution is low or depleted. For many applications, this can significantly prolong the life of the electrode. Refillable electrodes allow the user to change the filling solution if it becomes contaminated. Users can also change the filling solution for specialized applications if necessary, for example when measuring pH in organic solvents.

A common misconception is that refillable electrodes are more precise than sealed electrodes. However this is not the case, as highly precise, sealed electrodes are available that offer comparable or more precise readings than refillable electrodes. One example is the ROSS™ polymer-filled sealed electrodes which offer precision of 0.02 pH units. By comparison, most refillable electrodes offer a precision of 0.01 to 0.02 pH units.

Single-Junction vs Double-Junction

In combination electrodes, the reference junction allows H ions to pass freely between the reference and sensing half-cells to complete the electrical circuit. The most common junctions are made from a ceramic material and come in either single or double format. Economical single-junction electrodes are ideal for general-purpose applications and cleaner water applications. They are typically not recommended for use with samples containing proteins, organics, heavy metals, sulfides, Tris buffers, or any other biological media. These samples will react with the trace amount of silver that is present in the electrodes. Double-junction electrodes are recommended for these applications because they have an extra barrier which prevents this reaction. Double-junction electrodes also tend to last longer for many applications because of this extra barrier.

Although most reference cells feature an H -permeable glass junction, electrodes with reference junctions made of PTFE are also available. Electrodes with PTFE junctions are better suited for use with solutions that are highly viscous or those that have particulates which clog conventional glass junctions. These applications may involve measuring oils, paints, pastes, or inks.

A variety of specialized electrode junctions for specific applications are also available:

- **Flushable Junction/Sure-Flow® Electrodes**

  – ideal for viscous or dirty samples; junction is flushable and will prevent clogging and exhibit faster response times due to constant flow of fill solution into the samples being measured. It is good for all sample types even highly viscous samples though a high leak rate will require more frequent refilling.

- **Glass Capillary/Open Pore Electrodes**

  – provide a larger junction and an increased flow for a more stable junction potential.

- **Wick Junction Electrodes**

  – typically made of glass fibers, fiber optical bundles, or Dacron®. These are used in epoxy body electrodes for aqueous samples. They exhibit a slow response time and will clog if samples are too dirty or viscous.

- **Ceramic Junction Electrodes**

  – Made of porous ceramic, wooden plug, or porous PTFE. This is the most common junction found in a standard laboratory. Ceramic junction electrodes will clog if samples are too dirty or viscous; they are used in glass body electrodes.

Reference Type Electrodes

Silver/Silver Chloride (Ag/AgCl)

Ag/AgCl is the most common internal element in this type, suitable for almost all applications (their temperature limit is 176°F (80°C).

Another reference type is the Thermo Scientific™ ROSS™ electrodes. This reference type features a redox couple iodide/iodine (I_2/I) internal reference. The iodide/iodine internal reference combined with a platinum wire creates a redox

potential. This allows for a faster response and better stability over time than an electrode with a silver wire and the traditional Ag/AgCl complex fill solution. However all refillable ROSS electrodes will use a 3M KCl outer reference solution.

Temperature Measurement and Temperature Compensation

As with any pH measurement, consider the temperature measurement when choosing the correct electrode for the application. The pH of a solution can vary greatly depending on the temperature of the solution and any temperature change in the sample will also affect the readings.

Almost all meters feature either manual or automatic temperature compensation as a standard feature. Manual temperature compensation requires the user to manually enter the measured temperature value of the sample being measured. Automatic temperature compensation or ATC continually measures the temperature and corrects for changes in an electrode and readings due to a change in the temperature of the solution. It does require an additional probe to measure the temperature.

Choose from two probe options when using a meter with ATC. One option is to use a separate temperature probe from your pH electrode. The type of connection for the ATC probe is specific to the brand and model of the meter so consider this when making a selection. The major benefit of using a separate temperature probe is that it provides your meter with the flexibility to accommodate many different types of pH electrodes. This is convenient for various application changes or when accommodating different types of samples. The ATC probe also doesn't need to be replaced when the pH electrode goes bad.

The second option is using a pH electrode with an ATC element integrated. This type of electrode is referred to as an all-in-one or three-in-one electrode. All-in-one electrodes are more convenient because only one probe enters the sample. Because these probes have both the pH and the ATC electrodes in one unit, there are usually two connectors. One connector will typically be a standard BNC connector for the pH portion of the electrode. The other connector will be the temperature connector of the electrode that is specific to the brand of pH meter. Choosing an all-in-one electrode may reduce the number of electrode options available for the meter. Custom solutions are available if requested. Many handheld pH testers incorporate both the pH and ATC electrode into one unit as well. pH testers are meters that are designed for field and more rugged applications.

Connection Type

A variety of different pH electrode connections connect to a pH meter. Most pH electrodes come with a BNC connection. BNC probes will be compatible with a wide variety of meters, however, this doesn't apply for electrodes with built-in temperature compensation (ATC). Here is a list of the more common connection types:

- BNC – the BNC connection is the most common and universal electrode connection type
- DIN connector – This is still a relatively common connection and is usually for probes with a built-in ATC
- US standard – This is an older standard that is used less frequently
- Pin tip – This connection type was used mostly with half-cell electrodes which have been replaced with combination electrodes

In addition to the pH electrode, the ATC also has a specialized connection. ATC probes are less universal as most manufacturers use a different type of temperature sensor and connection type. Usually it is best to find the appropriate ATC

electrode by looking in the accessory section of the pH meters manual. Here are a few options:

- Mini DIN
- 8-pin DIN
- Cinch
- 4-pin
- RCA plug
- Phono jack (3.5 mm or other)

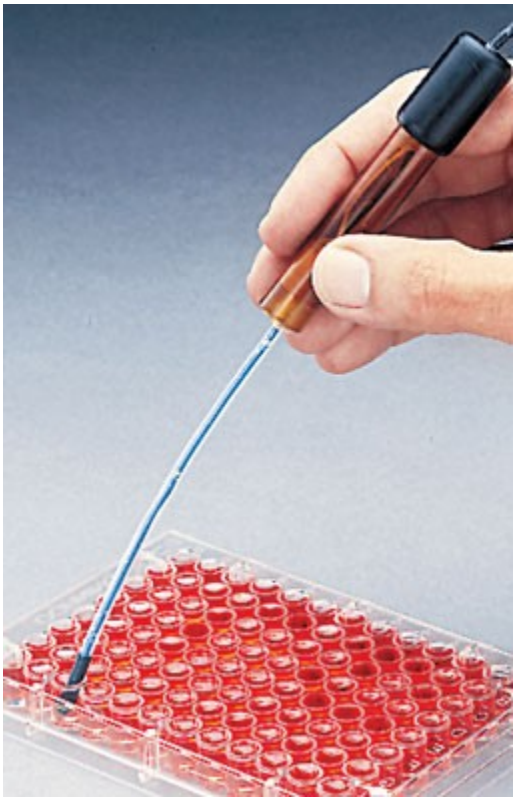
Specialty Electrodes

- Standard Electrodes – approximately 12 mm in diameter; typical lab electrode

- Narrow Electrodes – approximately 6 to 8 mm in diameter; extended length for use with bottles, vessels, and test tubes

- Semi-Micro Electrodes – approximately 6 to 8 mm in diameter; capable of measuring down to 200 µl sample size

- Micro Electrodes – 1 to 5 mm in diameter; capable of measuring down to approximately 0.5 µl; ideal for use with 384-well plates



• Rugged Bulb Electrodes – more robust design to prevent breakage; great for field use

• Spear Tip Electrodes – used for piercing solid or semisolid samples; cheeses, meats, etc.; good for small sample volumes

• Flat Surface Electrodes – used for measuring the pH of surfaces, solids, or gels; good for small samples volumes

• PerpHecT™ pH Electrodes – specifically designed for use with Thermo Scientific™ PerpHecT™ pH meters; LogR temperature compensation feature allows for simultaneous pH and temperature measurement without the use of a separate ATC probe.

• Antimony Electrodes – specifically designed for resistance to HF acid as they do not contain glass. These can generally tolerate up to 5% HF acid concentration. The major concern when using an antimony probe is that they have a different offset than standard probes. At pH of 7, the mV reading is around −400 mV ±30 mV, and the slope is around 50 mV/pH versus 59 mV. A meter that can compensate for this is required and may be more difficult to find.

Electrode Selection Guide for Identified Applications

- Biological samples – Double junction or ROSS electrode
- Pharmaceuticals – Double junction or ROSS electrode
- Hydrofluoric acid – Antimony or HF electrode
- Low ionic strength samples and acid rain – AccuFlow or Sure-Flow styles
- Boiler feed water and distilled water – AccuFlow or Sure-Flow styles
- Drinking water – Standard Ag/AgCl with single junction
- Wastewater – Double junction or ROSS electrode
- Solutions with heavy metals – Double junction
- Soil samples – Soil electrode or double junction
- pH >9 and High Na – Most single or double junction electrodes, Ag/AgCl
- High or rapidly changing temperature – ROSS styles
- Moist flat surfaces – Flat surface style
- Cheese, agar, paper, and skin – Flat surface style
- Semisolid samples – Spear tip, Ag/AgCl, ISFET
- Fruits, cheese, and meat – Spear tip, Ag/AgCl, ISFET
- Non-aqueous samples, solvents, and alcohols – AccuFlow styles, Sure-Flow styles, or Double junction
- Viscous samples, slurries, suspended solids, and sludges – AccuFlow styles, Sure-Flow styles, Double junction, or ISFET
- Emulsions and oils – AccuFlow styles, Sure-Flow styles, Double junction, or ISFET
- Paints and inks – AccuFlow styles, Sure-Flow styles, Double junction, or ISFET

The Electrode Pair

Sensing and reference half-cell electrodes must be used together to complete the pH circuit. Most of the electrodes in our catalog are combination electrodes that house both half-cells in a single probe.

Sensing Half-Cells

Sensing half-cells are the measuring portion of the electrode system and contain the pH-sensitive membrane.

Glass vs ISFET Sensors

The glass membrane or bulb of an electrode is constructed for use in specific conditions. Different types of glass membranes can strengthen the electrode, expand its temperature range, or prevent sodium error at high pH values.

- General-purpose glass: various pH ranges, temperatures to 212°F (100°C).
- Blue glass: pH 0-13, temperatures to 230°F (110°C)
- Amber glass: pH 0-14, temperatures to 230°F (110°C), low sodium (Na) error (In solutions with high Na concentrations, Na can be misread as H at pH 12 and higher.)

also offers solid-state ISFET (ion-specific field effect transistor) electrodes. The nonglass measuring surface won't break and wipes clean for dry storage—excellent for use in the food industry.

Epoxy vs Glass Body

Epoxy-body electrodes are impact resistant and ideal for rough handling, but should not be used at higher temperatures or for inorganics. Glass-body electrodes withstand high temperatures and highly corrosive materials or solvents.

Epoxy-body electrode

Glass-body electrode

Reference Half-Cells

Reference half-cells provide the reference potential needed for pH measurement. Our selection of electrodes includes a variety of reference cell options:

Single- vs Double-Junction

In combination electrodes, the reference junction allows H ions to pass freely between the reference and sensing half-cells to

complete the electrical circuit. Economical single-junction electrodes are ideal for general-purpose applications. Use double-junction electrodes with solutions that contain sulfides, heavy metals, or Tris buffers to prevent contamination of the reference cell.

Although most reference cells feature a H -permeable glass junction, electrodes with reference junctions made of PTFE are also available—use with solutions that may clog conventional glass junctions.

Silver/Silver Chloride (Ag/AgCl) vs Calomel (Hg/Hg_2Cl_2)

Ag/AgCl is the most common internal element, suitable for almost all applications [temp limit: 176°F (80°C)]. Hg/Hg_2Cl_2 is recommended for use in solutions containing proteins, organics, or heavy metals that could react with silver and clog the reference junction [temp limit: 158°F (70°C)].

Refillable vs Sealed

Refillable electrodes have ports that allow you to refill the reference chamber with reference solution—they are economical and long-lasting. Sealed electrodes are rugged and require virtually no maintenance; however, they must be replaced when the fill-solution level is low.

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