

Instructions

Combination pH Electrodes with Silver/Silver Chloride References

Glass Body Units/Liquid-Filled

Catalog No.	pH Range	Temperature Range (°C)	Temperature Range Intermittent (°C)
13-620-90	0 to 14	-5 to 110	
13-620-91	0 to 14	-5 to 110	
13-620-92	0 to 14	-5 to 110	
13-620-93	0 to 14	-5 to 110	
13-620-94	0 to 14	-5 to 110	
13-620-285	0 to 14	-5 to 110	
13-620-291	0 to 14	-5 to 110	
13-620-292	0 to 14	-5 to 110	

Polymer Body Units/Liquid-Filled

13-620-97	0 to 14	-5 to 80	-5 to 100
13-620-98	0 to 14	-5 to 80	-5 to 100
13-620-99	0 to 14	-5 to 80	-5 to 100
13-620-83	0 to 14	-5 to 80	-5 to 100
13-620-287	0 to 14	-5 to 80	-5 to 100
13-620-289	0 to 14	-5 to 80	-5 to 100

Polymer Body Units/Gel-Filled

13-620-104	0 to 14	-5 to 80	
13-620-106	0 to 14	-5 to 80	
13-620-108	0 to 14	-5 to 80	
13-620-109	0 to 14	-5 to 80	
13-620-110	0 to 14	-5 to 80	
13-620-252	0 to 14	-5 to 80	
13-620-290	0 to 14	-5 to 80	

Fisher combination electrodes offer the convenience of having the reference and measuring electrodes combined in a single housing. They are offered in a wide variety of configurations to meet most application needs.

Basically, the design consists of a glass pH indicating electrode coaxially joined to a silver/silver chloride reference electrode. The glass pH indicating electrode is located at the center of the probe. The reference electrode is located in the outer annular space of the probe. The outer annular space contains the silver/silver chloride reference element, electrolyte (4M KCl saturated with AgCl or gelled 4M KCl saturated with AgCl) and the junction (ceramic or porous plug). When immersed in a solution, the reference electrode makes contact with the sample through the junction thus completing electrical contact between the reference electrode, sample and pH indicating electrode.

Fisher combination electrodes are responsive over the full 0 to 14 pH range. Glass body liquid-filled units are available in standard and micro sizes, and are recommended for most routine applications. Polymer body liquid-filled units are available in standard and micro sizes and are recommended for applications where breakage is a problem. Polymer gel-filled units are available in both standard and micro sizes and are best suited for those applications where there is a need for both low maintenance and breakage resistance.

INSTALLATION

To place the combination electrode into service perform the following:

CAUTION: Polymer-bodied electrodes should not be used in non-aqueous solvents, concentrated acetic acid or concentrated oxidizing agents.

I. Liquid Filled Units

1. Carefully remove the plastic cot from electrode. Save the cot for future storage. Always exercise care when handling the electrode, since a slight scratch on the glass bulb can render the electrode useless.
2. Rinse the electrode with distilled water to remove crystal residue that may have formed on the surface during storage. (The residue is caused by the natural leakage and gradual evaporation of electrolyte during storage.)
3. If the fill hole is located on the cap ring, rotate the hole from the closed to the open position. If the fill hole is located on the electrode body, lower the rubber sleeve and remove the white vinyl tape to expose the fill hole.
4. Check the electrolyte level in the reference cavity (outer annular space). If the fill hole is located on the cap, the electrolyte level should be approximately $\frac{1}{4}$ inch below the cap. If the fill hole is located on the body, the electrolyte level should be approximately $\frac{1}{4}$ inch below the fill hole. If the electrolyte level is too low add electrolyte from the provided bottle of Fisher No. SP135 (4M KCl saturated with AgCl).
5. Proper electrode function requires electrolyte flow at the junction. To ensure adequate flow, perform the following procedure:
NOTE: The liquid junction is located on the side of glass bodied units (white ceramic dot) and in the silicon bung at the base of the electrode on polymer bodied units (white ceramic rod or dot).
 - a. Hold the electrode upright at a 45° angle between the thumb and the forefinger of the left hand, so that the filling hole faces out and is directly opposite the base of the thumb.
 - b. Insert the spout of the electrolyte dispensing bottle into the fill hole.
 - c. Making sure that the electrode is supported by the base of the thumb, firmly press the spout into the fill hole to make an airtight seal.
NOTE: Normally, the spout tip will not touch the internal element. While applying pressure, care should be exercised to prevent contact with this element. If contact occurs, it will be necessary to cut off a small portion of the tip.
 - d. While maintaining the seal, squeeze the filling bottle so that the electrode becomes pressurized. A bead of liquid should form at the liquid junction in about 30 seconds; in some cases it may be necessary to maintain pressure for several minutes.
6. Mount the electrode on a suitable holder and connect the jack/jacks to the meter.
NOTE: If the electrode was supplied with a removable plastic bulb protector, it can be placed on the electrode at this time.



7. Allow the electrode to soak in buffer for 10 minutes prior to standardization.
8. Check the electrode response.
 - a. Using a one-point standardization, proper response is indicated if the error is less than ± 0.05 pH per pH unit from the standardization point when using fresh Fisher certified ± 0.02 pH buffers.
 - b. Using a two-point standardization, an efficiency > 0.95 or slope $> 95\%$ indicates proper response.

II. Gel-Filled Units

1. Carefully remove the plastic cot from the tip of the electrode. Save the cot for future storage. Always exercise care when handling the electrode, since a slight scratch on the glass bulb can render the electrode useless.
2. Rinse the electrode to remove any crystal residue that may have formed during storage.
3. Remove the excess water on the electrode by shaking the probe.
4. Mount the electrode on a suitable holder, and connect the jack/jacks to the meter.
NOTE: Since the bulb is protected, the electrode may be placed directly into the solution and used to stir the solution to enhance response time.
5. Allow the electrode to soak in buffer for 10 minutes prior to standardization.
6. Check the electrode response.
 - a. Using a one-point calibration proper response is indicated if the error is less than ± 0.05 pH per pH unit from the standardization point when using fresh Fisher certified ± 0.02 pH buffers.
 - b. Using two-point standardization, an efficiency > 0.95 or slope $> 95\%$ indicates proper response.

OPERATION

For optimum operation observe the following precautions.

I. Liquid Filled Units

1. The fill hole must be open when taking measurements.
2. The electrode need only be immersed far enough to cover both the glass pH sensing bulb and reference junction to obtain accurate readings.
3. The level of electrolyte in the outer cavity must always be kept above the level of the solution being measured.
4. The level of electrolyte must always cover the reference element; otherwise electrical contact cannot be established. Add electrolyte as needed. (See INSTALLATION procedure.)
5. Always rinse the electrode with distilled water between samples.
6. To optimize electrode life avoid prolonged measurements in strong alkaline solutions.
7. Due to the high impedance (resistance) of the pH glass membrane, the electrode cable should not be moved or touched while measurements are being made; otherwise unstable readings may result.

II. Gel Filled Units

1. The electrode need only be immersed far enough to cover both the glass pH sensing bulb and the reference junction to obtain accurate readings.
2. Always rinse the electrode with distilled water between samples.

3. To optimize the electrode life avoid prolonged measurements in strong alkaline solutions.
4. Avoid taking measurements in samples with widely varying temperatures. Failure to do so may shorten electrode life due to contamination of the gel with sample.
5. Due to the high impedance (resistance) of the pH glass membrane, the electrode cable should not be moved or touched while measurements are being made; otherwise unstable readings may result.

STORAGE

1. Never store the electrode in distilled or deionized water. This may lead to slow sluggish response caused by junction clogging.
2. Between measurements immerse the electrode in a buffer solution (4 or 7 recommended). For liquid filled units keep the fill hole open to avoid contamination of the electrolyte from the buffer solution.
3. When the electrode is not in use, it is highly recommended that the plastic cot be replaced over the probe tip. Wet the cotton inside the cot with pH 4 or 7 buffer. Then while squeezing the cot place it over the tip of the probe and slide it on. This procedure keeps the probe in a ready state. (Close the fill hole on liquid filled units.)

REJUVENATION

pH electrodes will naturally age and undergo a reduction in their Nernstian response. Occasionally, this is accompanied by sluggish response. This aging is caused by either contamination of the glass membrane or by clogging of the liquid junction. (In rare instances, poor response can be caused by a deterioration of the insulation between the shield and the internal element.) Separate procedures are given below for cleaning the glass membrane surface and unblocking the junction.

CLEANING THE GLASS pH MEMBRANE

A dirty glass membrane is usually indicated by beads of water forming on the bulb when it is rinsed with distilled water. The bulb can be cleaned as follows:

1. For protein layers — soak in a freshly prepared solution of pepsin in 0.1N HCl (approximately ¼ teaspoon/100 ml) for 30 minutes.
2. For inorganic deposits — wash with EDTA, ammonia, or acids.
3. For grease and similar films — wash with acetone, methanol, etc.

UNBLOCKING THE JUNCTION

If the junction should become blocked or partially plugged, perform the following:

I. Liquid Filled Electrodes

1. Inspect the reference cavity for crystallization. If crystallization is present, go to step 2; if not, proceed to step 3.
2. Remove crystals as follows:
 - a. Remove the filling solution by shaking it out through the fill hole.
 - b. Repeatedly rinse the reference cavity with distilled water until all crystals are dissolved.
 - c. Empty the reference cavity and refill it with SP135.
 - d. Pressurize the electrode (see step 5 under INSTALLATION) and determine if flow is re-established. If no flow is found, proceed to step 3.

3. Perform the following procedures in sequence and as needed, depending upon the severity of the blockage.
 - a. Soak the electrode tip in warm water and apply pressure to the filling hole (see step 5 under INSTALLATION).
 - b. Soak the electrode tip in concentrated ammonium hydroxide for 5 to 10 minutes (use adequate ventilation and precautionary measures). Rinse with deionized water. Then, apply pressure to the filling hole (see step 5 under INSTALLATION).
 - c. If the junction remains clogged, you may carefully sand or file the porous plug on glass-body units, making certain not to contact the glass bulb.

II. Gel-Filled Electrodes

Perform the following procedures in sequence and as needed, depending upon the severity of the blockage.

1. Soak the electrode in warm water (approximately 60°C) for 5 to 10 minutes. This should re-establish contact.
2. Place the electrode in warm, saturated KCl solution (approximately 60°C) and allow the electrode and solution to cool to room temperature.

RECONDITIONING THE SENSING MEMBRANE

Prolonged use, excessive alkaline immersion, or high temperature operation will cause surface leaching of the membrane glass, resulting in extremely noisy and/or sluggish response which cannot be remedied by the steps outlined above. If this occurs, the following procedures will often provide renewed stability and pH sensitivity:

1. Immerse the electrode tip into 0.1M HCl for about 15 seconds; rinse the water, and immerse into 0.1M KOH for 15 seconds. Cycle the electrode through these solutions several times; then, recheck the electrode performance. If problem still persists, go to step 2.
2.
 - a. Immerse the electrode tip into a 20% ammonium bifluoride solution for 30 seconds or a 10% hydrofluoric acid solution for 15 seconds.
WARNING: The above fluoride solutions are extremely corrosive and hazardous, and proper safety procedures must be observed when handling and using them.
 - b. Thoroughly rinse the electrode with water, then immerse the electrode tip into concentrated hydrochloric acid for 30 seconds to remove any residual fluorides and rinse again with water.
 - c. Soak the electrode in buffer (pH 4 recommended) for at least 1 hour. Then recheck electrode performance. If performance has not been restored, the electrode should be replaced.

NOTE: Frequent fluoride treatment can shorten the electrode life and may eventually cause membrane cracking.