Selection and care of pH electrodes

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CHOICE of pH electrodes depends on the application, the sample size, and the shape and size of the sample container. Individual glass and reference electrodes can be used in a pair or combined in an integral probe. This article outlines the basis for selection of electrodes and what is required to maintain them.

Types of electrodes

Electrode pair

The pair of individual electrodes has the advantage of flexibility in choice of reference type and junction. Since there is no junction type which is universal or applicable to all sample types, this is a distinct advantage. For example, the sleeve junction reference is excellent in viscous or colloidal samples since it provides high flow rate and is easy to clean, whereas other types may become clogged easily. Another advantage of an electrode pair over a combination electrode is the lower expense in replacement if breakage of one electrode occurs.

Combination electrode

The combination electrode may be preferred over the electrode pair because of limited sample size and sample container configuration. With the reference and glass electrodes combined into a single probe, it is possible to measure samples as small as 100 μl in a centrifuge tube or to measure samples in tall flasks. With the reference junction close to the glass bulb, noisy reading caused by high sample resistance is less of a problem. An annular ceramic junction, which surrounds the glass bulb, often has lower junction potential than a single junction since it consists of numerous junctions. This provides less drift and better response.

Glass electrode

The main criteria of the glass electrode are pH range, span, and response. Some glass electrodes are made with the full pH range 0–14. Others produce significant error above pH 11 due to sensitivity to sodium ion. For example, about ½ pH unit error will be observed in a 0.1 *M* Na^+ solution at pH 13 at 25°C with a general-purpose-type bulb (0–11 pH).

A general-purpose glass is preferred for use below pH 11. It will provide faster response and greater stability than the full-range glass, since it is lower-re-

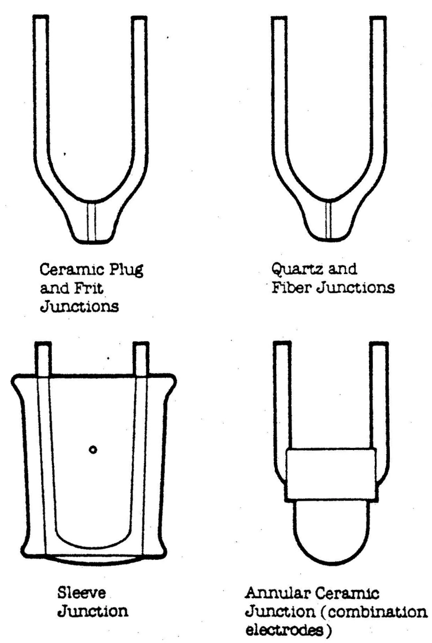

Figure 1 *Various configurations of junction type electrodes.*

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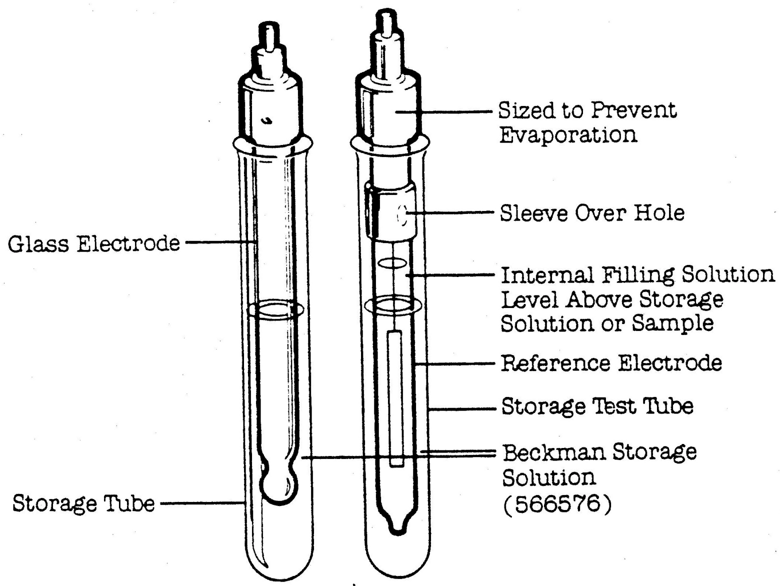

Figure 2 *Storage of electrodes.*

sistance glass. At pH values above 11, however, the full range provides lower sodium ion error than the general-purpose glass.

Reference electrode

Of the hundreds of different types of reference electrodes that have been produced, only a few are commonly used. Various configurations of junction types are shown in *Figure 1*.

The critical part of a reference electrode is its junction. A clogged or high resistance junction is responsible for most pH measurement difficulties. Therefore, its selection is critical for stable and accurate measurement.

Performance of various junctions can be rated by drift and stabilization time in different solutions. A study has been conducted to categorize performance of different junctions in various types of solutions. The general overall performance in most samples was excellent. Preferences, however, could be established for a few types of solutions for which the junction exhibited different performance. For example, the ceramic junction required a longer stabilization time and drifted more in strong acid than did the quartz junction.

The reference junction performs best when it has the least liquid-junction potential. This most often occurs with a fast flowing, low resistance junction. However, the fast flow of electrolyte from the reference electrode may be undesirable because of significant contamination in small volume samples. If a large volume sample is being measured, the sleeve junction is normally the best junction. If lower flow rates are desired, either the annular ceramic on the combination electrode or the quartz junction is a good choice. In some cases, a salt bridge and salt bridge solution may be necessary to prevent chloride or potassium contamination from the liquid junction.

Either the calomel or silver-silver chloride internal reference electrodes provide excellent potential stability. The silver-silver chloride electrode provides slightly more stable potential at high temperatures (>50°C). The filling solution that surrounds the calomel internal reference electrode is saturated with silver chloride. In some cases, such as kinetic measurements, this small amount of silver may interfere by reacting with the enzyme. (More information about selection of a reference electrode can be obtained from the author.)

Electrode style

Another consideration in choice of electrodes is integral (standard) or detachable (Beckman Futura) style cables. Integral cables have two advantages: They don't get lost, and they don't require contacts to be cleaned. Detachable cables provide choice of length, easy storage, and autoclavability. Also, the electrode without the cable is less expensive to replace.

Care of electrodes

Storage

The glass electrode should be stored in a slightly acidic solution to obtain faster response than occurs with neutral or low ionic strength storage solution.

The reference electrode should be stored in 0.1 *M* KCl solution. Keeping the junction wet is essential for keeping it unclogged. The filling solution level should be kept significantly above the storage or sample solution level in order to provide a positive head pressure, thereby forcing filling solution out through the junction. See *Figure 2*.

A combination electrode should be stored in a slightly acid 0.1 *M* KCl solution: in other words, a combination of the glass and reference storage solutions.

Glass electrode rejuvenation

The pH electrode may be rejuvenated by immersing the tip momentarily in 0.1 *N* HCl, or alternately immersing the tip in acid and alkali (cycling); this also reduces residual sodium ion effects. If acid treatment or cycling fails to rejuvenate the electrode, the tip can be immersed in 20% ammonium bifluoride solution for 3 min, or in 10% hydrofluoric acid for no more than 15 sec.

Electrodes can be rejuvenated as often as necessary. However, frequent rejuvenation will reduce electrode life and may cause the immersion tip to crack. After acid fluoride rejuvenation, the electrode should be rinsed in a stream of tap water, dipped momentarily in 5 *N* hydrochloric acid to remove fluorides, and then rinsed again in tap water. The rejuvenated electrode should be stored in electrode storage solution. The electrode tip may be coated with Desicote, a silane-based product, to minimize sample carry-over and to aid in rinsing between samples.

Unclogging a reference electrode

The reference junction is normally the source of most difficulties encountered because of high resistance and high junction potential. In order to free a junction and lower its resistance:

1. Replace the filling solution.

2. Soak the junction overnight in 0.1 *M* KCl solution.

3. Apply pressure to the filling hole or vacuum to the junction tip.

4. Boil the junction for 10 min in dilute KCl solution.

5. As a last resort, sand the junction tip with 600 emery paper.