Orion pH, ORP and ISE Theory

Choosing the Correct Reference System

Three criteria apply when you choose a reference electrode:

- The reference electrode should provide a stable and reproducible potential under a wide variety of sample conditions
- The reference electrode filling solution should not interfere with the sensing electrode. Ions that interfere with the analyses should not be introduced into the sample by the reference electrode
- The filling solution should flow freely with no fouling or plugging of the junction by the sample

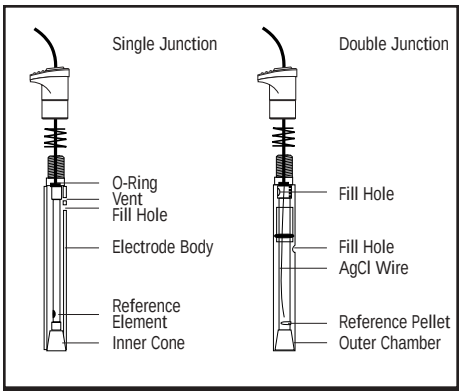
Reference Electrode for Half-Cell Systems

Half-cell reference electrodes help complete the measuring circuit when using a half-cell sensing electrode. Thermo Electron recommends two types of reference electrodes, both include the sleeve-type Orion Sure-Flow® reference junction. The Sure-Flow junction provides many benefits, including working in dirty or viscous samples without clogging. The simplest sleeve reference is a single junction type, which uses a filling solution saturated with silver (in the form of silver chloride) to satisfy the requirements of the internal cell. The double junction type is useful when the fill solution of a single junction electrode contains an ion that interferes or reacts with the ion being analyzed. For example, use of potassium chloride fill solution is undesirable for a chloride analysis because the fill solution introduces more chloride into the sample and leads to falsely high results. The double junction electrode allows for selection of a non-interfering solution to contact the sample. In the case of chloride analysis, potassium nitrate, which causes no interference, may be used as a filling solution. Double junction electrodes also allow some additional fill solution choices when analyzing unusual samples that could cause changes in liquid junction potentials.

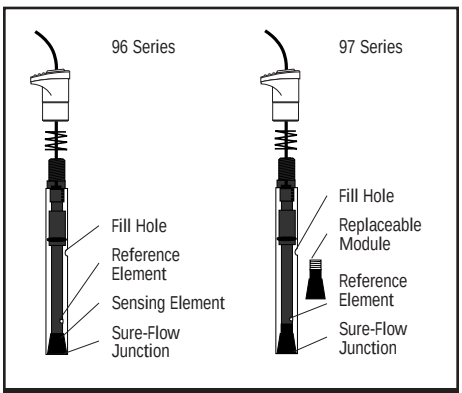
Combination Reference Electrode Systems

Half-cell systems use all purpose reference systems, which may not provide the needed performance under some application conditions. With combination electrodes, the built-in reference system meets all of the criteria for a reference electrode. Orion combination electrode designs provide an optimum reference system for the specific ion of interest. In the case of pH electrodes, combination electrode designs allow for unique electrode constructions for measuring flat surfaces, small samples in test tubes or piercing solid samples and septa. Orion's Sure-Flow junction design, on many pH and ISE combination electrodes, improves electrode performance because the sleeve construction allows a unique form flow rate of reference filling solution into the sample. The uniform flow rate produces stable reference potentials for faster response and better stability. In addition, the electrodes are cleaned by simply opening the reference junction.

Another reference system from Thermo is found in the Orion AquaPro electrode line where a high performance polymer isolates the Ag wire from the sample. These patented double junction, low maintenance electrode systems offer fast response due to an open junction. They are an ideal replacement for calomel electrodes as they do not contain mercury and the isolated reference allows them to be used with biological applications. AquaPro electrodes also offer excellent performance in dirty samples.



Reference Electrodes



Combination Electrodes

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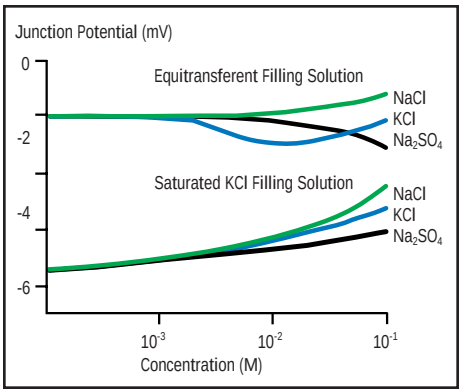

Liquid Junction Potential

Typical Applications

Salt	Concentration	Use
KCl	Saturated or 4 M	Generally useful except where K^+ and Cl^- must be absent
Na^+, K^+ Cl^-, NO_3^-	Orion equitransferent solution	Generally useful. Lower junction potential than saturated KCl in dilute (>10^{-3} M) ionic strength samples. Above 0.5M ionic strength KCl is preferable
KNO_3^-	Saturated	Trace Cl^- determination

Reference Junction Material

Orion pH electrodes are constructed with a variety of reference junctions, such as ceramic, wick, fiber or Sure-Flow®, based on the material of the electrode and intended application. A pH electrode whose junction material is compatible with the sample should be used. For most clean, aqueous samples, any junction type is acceptable. However when measuring dirty samples, the Sure-Flow junction is always recommended. Refer to pages 21, 61 and 62 for more information on choosing a pH electrode with an appropriate reference junction. Most Orion ISE combination electrode systems and half-cell systems employ the Sure-Flow junction for measurements in any sample type.

Liquid Junction Potential

A liquid junction potential develops at the reference electrode junction where the sample and filling solutions mix. Changes in liquid junction potentials can cause errors during electrode determinations. The liquid junction potential should be minimized for accurate measurements. In routine pH measurements liquid junction potential errors are not noticeable. It would take a change of 6 mV in potential to cause a noticeable difference at 0.1 pH, but liquid junction potentials are seldom of that magnitude. However, many ISE determinations are made to 1-2% accuracy. This situation could be altered by a typical liquid junction potential difference between the sample and standard of 0.1-0.2 mV. Junction potentials arise when ions in solution move at different rates. This occurs, for example, when sodium iodide diffuses into a less concentrated solution. The iodide ion, which is larger, moves more slowly compared to sodium. Consequently, sodium leaves iodide behind to build up charges that are added to the reference potential. Since the charge is not due to the ion of interest, a measurement error results. Mechanically, to avoid build-up of sample ions inside the junction, it is necessary to have a small continuous amount of reference filling solution flow out into the sample. The flow must be just fast enough to overcome back diffusion of sample ions into the junction. The electrode that best satisfies the above requirement is one that uses a sleeve junction reference, such as the Orion Sure-Flow junction. This reference ensures continuous flow as long as the analyst is careful to maintain a higher level of filling solution in the reference electrode compared to the sample level. The Sure-Flow reference electrode offers the added advantage in that it can be quickly flushed in case of contamination.

Reference Filling Solution

The most important variable the analyst can control is the composition of the reference filling solution. If the analyst has the Orion Sure-Flow double-junction reference electrode, the optimum solution for each particular application may be selected. Orion Optimum Results™ application solutions offer another aspect of control for the analyst. These reference filling solutions are used with Orion ionplus® combination ISEs. Each solution formulation is designed to provide a minimal junction potential for the particular application (patent pending). By reducing the effects of sample temperature changes, Optimum Results solutions enhance the electrode stability and response time to improve measurement accuracy.