pH

Introduction

pH is a measure of the hydrogen ion activity in a solution and is defined as:
$-\log_{10} a^{H+}$ where a^{H+} is the activity of the hydrogen ion. Practically, this means that at pH 0, the hydrogen ion concentration is 1×10^{14} times greater than at pH 14. This also means the hydroxyl ion concentration at pH 14 is 1×10^{14} times greater than at pH 0. When the hydrogen and hydroxyl ions are present in equal numbers (the neutral point), the pH is 7. Values from pH 0 to pH 7 are termed Acidic and those from pH 7 to pH 14 are termed Basic. It is important to note that a pH change of one unit (for instance, from pH 6 to pH 7) actually is a factor-of-10 change (decade difference) in the hydrogen ion concentration.

The pH electrode used in pH measurement consists of a glass sensing half-cell and a reference half-cell. Together the two half-cells form an electrode system. The sensing half-cell is a thin pH-sensitive glass membrane separating two solutions. The outer solution is the sample to be tested. The internal solution is enclosed within the glass membrane and has a known pH. An electrical potential is developed on the inside surface of the glass membrane with the internal solution and remains constant. Another electrical potential is developed on the outside surface of the glass membrane with the sample solution. This potential varies with the pH of the sample solution. The amount of variation is linear when the temperature is constant. The change in potential per pH unit is termed the Electrode Slope.

A second half-cell, or reference half-cell, in contact with the sample solution has a constant potential. Therefore, any changes in the potential of the electrode system at a given temperature will be due to changes in the pH of the sample solution. Sensing and reference half-cells may be contained in two separate electrodes, or they may be combined and called a combination electrode; see the *Platinum series combination electrode* figure.

Temperature effects on pH measurements depend on the reference electrode used, pH of the solution within the pH electrode and pH of the test solution. At a certain pH, temperature will have no effect on the potential of the electrode system. This is known as the isopotential point. Also, at some pH level, the system will exhibit 0 millivolts. This is known as the zero potential point. Both the isopotential and zero potential points are features designed into electrodes. Hach electrodes are designed so the isopotential and zero potential points are at pH 7. This minimizes temperature effects in the majority of typical samples.

Conventional electrode design

The porous junction of a conventional reference half-cell is made of ceramic or fiber. With time, the junction will become clogged with silver chloride or contaminants, causing large variation in the reference potential. In addition, reference solution can be contaminated or diluted by back diffusion of sample into the junction. Particular contaminants may be introduced into the junction. Clogged or fouled junctions can cause drift along with inaccurate, noisy, erratic and sluggish pH measurements. The performance of conventional porous junctions deteriorates as they age because of clogging; see Figure 1.

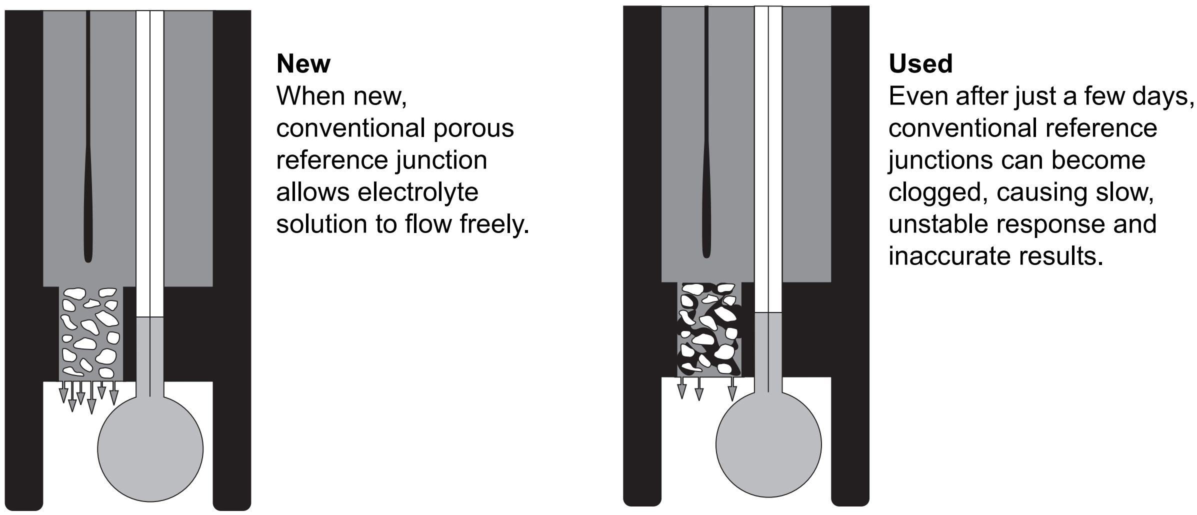

Figure 1 Conventional combination electrode

Platinum series electrode design

Platinum Series Electrodes solve this clogging problem because they use a continually renewed liquid junction, also known as a free diffusion junction (FDJ); see Figure 2. There is no ceramic or fiber plug to become clogged and therefore the electrode lasts longer. The free diffusion junction has been shown to have a faster and more stable response than conventional electrodes (Figure 1). Figure 4 shows the accuracy and stability of the Platinum Series Electrode.

Figure 5 shows the variation of the Platinum Series Electrode and a conventional electrode. The Platinum Series Electrode clearly provides repeatable results.

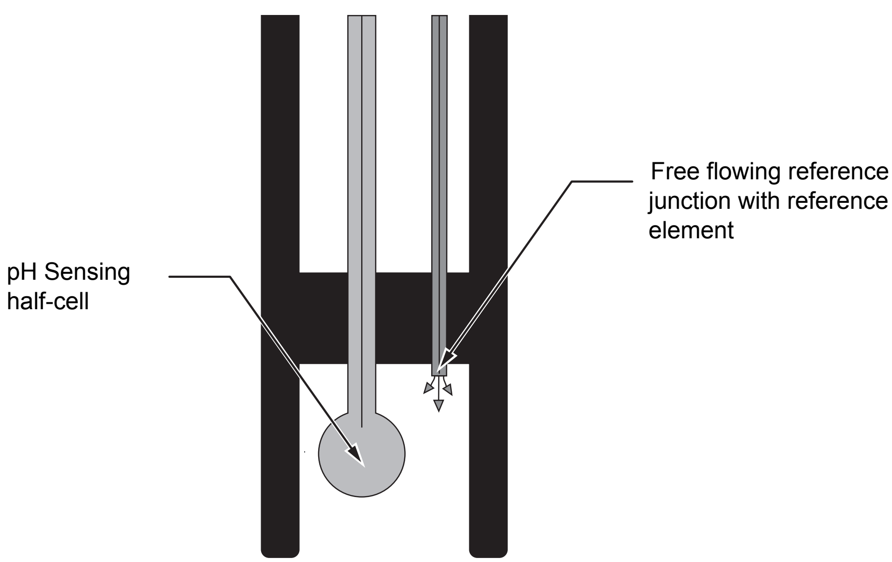

Figure 2 Platinum series combination electrode

Note: *The free-flowing reference junction design prevents clogging. Every measurement is rapid, accurate and stable, regardless of electrode age.*

The Platinum Series Electrode provides stable results in one minute in this deionized water sample. The conventional ceramic frit junction electrode shows a slow, noisy response.

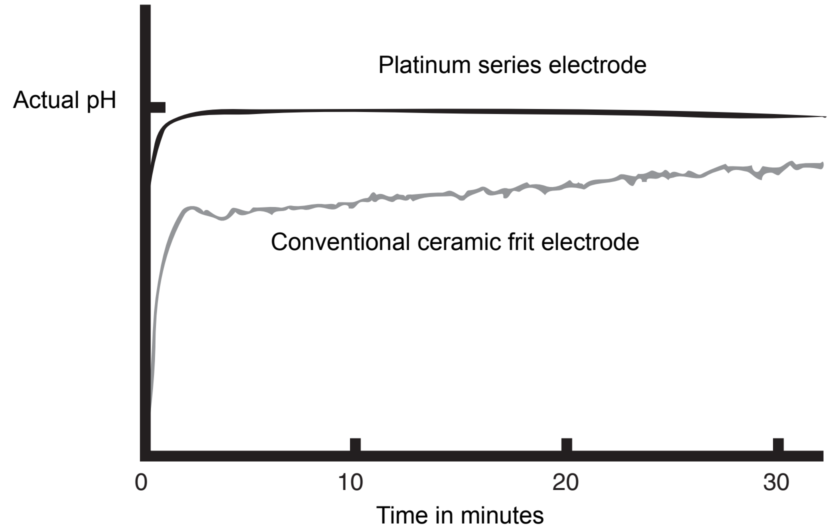

Figure 3 Response times and electrode drift for Platinum Series and conventional electrodes

The initial pH reading obtained with a conventional reference junction for a deionized water sample was incorrect, and shifted by 0.36 pH units when the sample ionic strength was increased by adding 50 mg of ultrapure KCl. The same electrode with a Platinum Series reference electrode showed significantly improved stability and accuracy.

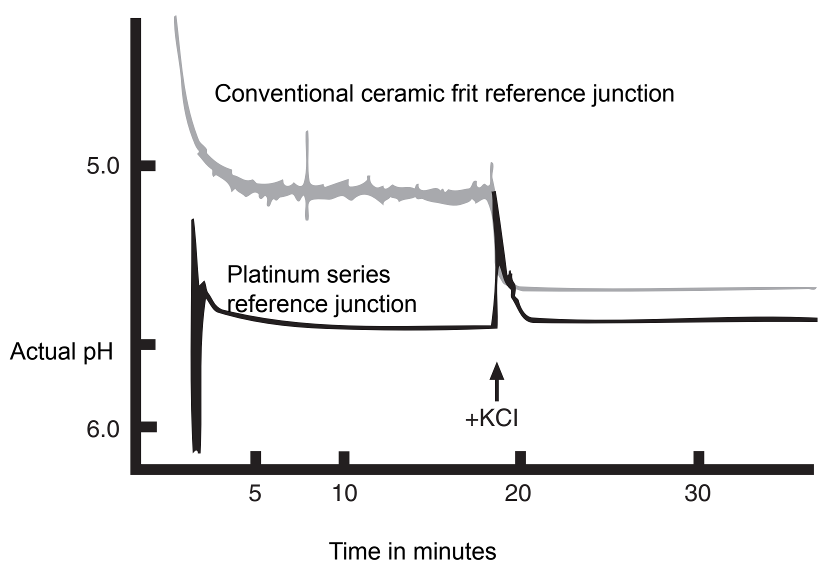

Figure 4 Accuracy of Platinum Series and conventional electrodes

Platinum series pH systems (white) provide repeatable results every time. The conventional electrode (gray) varies greatly from one measurement to the next.

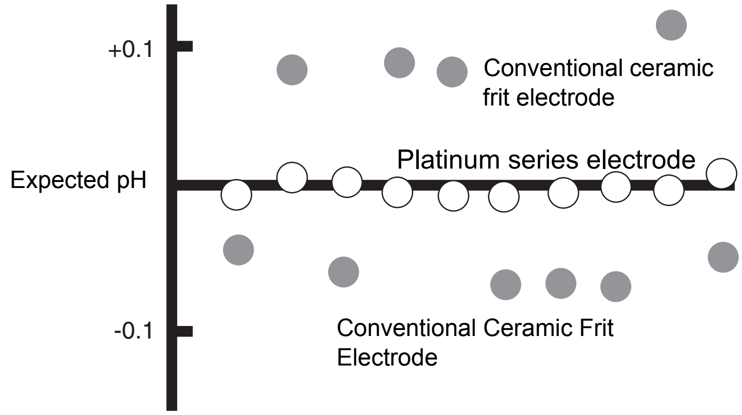

Figure 5 Repeatability comparison between Platinum Series and conventional electrodes