by Bob Taylor - Chemist for Flairform Australia

pH Meter Maintenance

Electronic pH Meters

pH meters employing a glass electrode are useful for precise pH measurement but require frequent calibration, proper storage and handling to ensure accuracy and reliability. The principle on which such meters operate is based on the fact that when glass of a certain composition separates two aqueous solutions having different hydrogen ion concentrations, a voltage is developed between the two faces of the glass. The electronic meter itself is simply a very sensitive voltmeter, which measures that voltage but is calibrated in terms of pH units instead of volts.

Figure 1: Popular styles of pH meters: availability ranges from the more expensive laboratory grade (left), to the cheaper pocket sized (right).

Calibration of pH Meters

To ensure their accuracy, pH meters must be regularly calibrated for accuracy using standard pH buffer solutions that are made to an internationally agreed recipe. These are stable solutions that possess a specific pH value. It is essential to calibrate using at least two pH buffers that differ in pH by at least three pH units over the range being used. For hydroponics pH buffer 4.0 and pH buffer 7.0 are the ideal calibration standards to use.

Some manufacturers claim their pH meters require only a single point calibration. However, that claim is simply not justifiable if accuracy is desire. The use of two pH buffer standards ensures that the calibration slope is obtained. If this precaution is not taken when the electrode is later placed in a pH buffer 4.0 solution, the meter will typically read, for example, 4.4, instead of 4.0. This potential problem can be avoided by using both the pH 7.0 and 4.0 buffers.

How to Calibrate

Follow your pH meter manufacturer's instructions. Alternatively, ensure to calibrate first with pH buffer 7.0 followed by pH buffer 4.0. To do this, rinse the electrode in distilled water and gently shake off the excess water. Then, immerse the electrode in pH buffer 7.0 solution for at least two minutes before adjusting so that it reads 7.0. Finally repeat the procedure with pH buffer 4.0 adjusting so that it reads 4.0. To prevent contamination of the pH buffers, decant a portion into a smaller container to perform the above calibration, and discard once used.

Common Mistakes Made When Using Electronic pH Meters

1. Before measuring the pH, ensure that the nutrient is well stirred, especially after pH up and down are used. This is one of the most common mistakes made when testing pH or conductivity. Also, ensure the sampling container is clean.
2. *See Figure 2* - When the pH electrode is placed in a sample, you may notice that the reading varies for some time (maybe several minutes) before resting on a final value. There may be a difference in excess of 1.0 pH unit between the initial and final pH value. Since the final value will be the most accurate, make sure you wait long enough for the reading to stabilize. However, note the section on cleaning.

Figure 2:
Stir nutrient tank well before sampling. Then leave the electrode in the sample for a few minutes before switching the meter on and taking the measurement.

3. Do not immerse the electrode in the sample to a depth that exceeds the level of the filling solution inside the electrode *(Figure 3)*. Since it is not possible to view the depth of the filling solution in many pocket sized meters, immerse the electrode to a depth of no more than 20 millimeters. Exceeding this depth can permit the sample solution to weep back into the electrode itself resulting in inaccurate readings.

Figure 3:
Do not immerse the electrode deeper than 20mm.

4. Once the reading has been taken, immediately remove the electrode from the sample and rinse with distilled water *(Figure 4)*. Failure to do so will cause rapid deterioration of the electrode and increase the need and frequency for routine maintenance – see section on cleaning. Whilst not in use, ensure to store the electrode *(Figure 5)* in a properly formulated storage solution – see section on storage.

Figure 4:
Always clean the electrode with distilled water after use - No. 1 maintenance tip for prolonged electrode life!

Figure 5:
Always keep pH electrodes immersed in a " storage" solution when not in use.

Accuracy problems with pH Meters

Note that despite being properly calibrated it has been my frequent experience that different pH meters will produce significantly different pH readings on the same solutions. This is especially true of lower quality electrodes because they can respond to other species that are electrochemically similar to hydrogen ions, such as sodium. For this reason a grower can get pH readings differing by more than 0.5 units when testing a nutrient sample with two different pH meters that have been correctly calibrated. Note that pH indicators cannot give false readings with colorless samples because they will only respond to hydrogen ions.

Storage of pH Electrodes

For a pH meter with a single combination electrode to work properly there must be an electrical connection between the electrode filling solution (usually potassium chloride – which is electrically conductive) and the sample solution. This is achieved

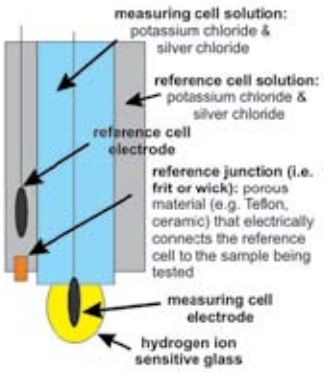

Figure 6: Schematic layout of glass pH electrode. Loss of accuracy is invariably explained by different degress of blockage of the 'frit' or 'wick' - often caused by dry storage. Testing of oily or harsh chemicals (eg. pH Up or concentrated nutrient), or failure to rinse the electrode properly after use.

via the use of a porous frit or wick *(Figure 6)* in the glass wall separating the inner filling solution chamber from the sample. Both these devices allow the free (very slow) flow of the filling solution into the sample solution.

The most common cause of pH meter failure is due to blockage of this porous frit or wick. This is usually caused by dry storage of the electrode or leaving the electrode immersed for too long in concentrated solutions. Dry storage causes dehydration of both the glass electrode and precipitation of salts within the interstices of the frit itself *(Figure 7)*. The consequences are reading drift, slow response times and decreased sensitivity resulting (loss of accuracy and precision). To avoid these problems the electrode tip must be permanently stored *(Figure 5)* in a specially formulated storage solution.

Note that water or pH buffers are not suitable for storage of pH electrodes.

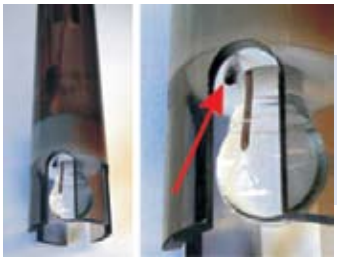

Figure 7: Arrow highlights contamination on this 'frit' (or wick). The hydrogen ion sensitive glass 'bulb' containing the measuring cell electrode can be seen to the right of the arrow.

Cleaning pH Electrodes

The frit and glass tip of pH meter electrodes invariably become contaminated with impurities (Fig 1.8b) causing symptoms such as reading drift, slow response times and decreased sensitivity (loss of accuracy and precision). Contamination may be so severe that re-calibration is not possible without prior cleaning. Minimize this problem by filtering potentially problematic water samples (i.e. greasy or highly turbid) prior to performing a pH measurement. Avoid placing electrodes in oily solutions as they can coat the electrode. Furthermore, avoid measuring (or leaving electrodes for too long) in harsh chemicals that are highly caustic (pH Up, silica additives) or concentrated solutions like raw nutrients. These can damage electrodes and/or increase the need for electrode maintenance.

Regular cleaning will maximize electrode performance and ensure a longer working life. Some suitable cleaners are:

- Organic contamination - use mild liquid detergent, acetone*, methylated spirit or toluol*. If toluol is necessary, rinse subsequently with acetone or methylated spirits and finally water.
- Inorganic contamination – use dilute nitric or hydrochloric acid.

In hydroponics, because both organic and inorganic contaminations tend to co-occur, it is best to use an all-purpose cleaner.

* Note that some cleaners may attack electrode hardware - particularly plastic. Therefore, ensure to check with the electrode's manufacturer before proceeding.

pH Indicators

Although pH indicators may not always distinguish between a pH of, say, 5.2 and 5.3, wide range color pH indicators having good color resolution can be:

- Fast
- Extremely accurate
- Simple
- Reliable
- User friendly
- Economical

As noted, pH meters require constant up-keep. Cleaning, calibrating and correct storage must be done on a regular basis, but even then may not give reliable readings. MY