INSTITUTE FOR HEALTH RESEARCH AND EDUCATION IHRE SIMON FRASER UNIVERSITY

website: http://ihre.sfu.ca

2812 West Mall Centre, 8888 University Drive, Burnaby, BC, Canada V5A 1S6

Dr. Andrew Lewis
Instrumentation Consultant

Cell: 604 721 4252
Email: arl@sfu.ca
E-Text: 6047214252@fido.ca

May 28, 2004

RE: pH Meter Use, Calibration, Maintenance and Cleaning

Instructions for Using pH Meters and Electrodes

There are several types of pH meter in use within the labs. All work on the same underlying principles, and have similar calibration and measurement protocols. In general, you will need the appropriate pH calibration solution(s) (buffer solutions made up to pH 4.00, 7.00, or 10.00), a glass pH electrode, and a suitable reference electrode (usually calomel or Ag/AgCl.) Note that some pH electrodes are combined with an appropriate reference electrode already. In all cases, please note the following:

- You should not place wet items or beakers of solution on the meters; similarly, try and avoid splashing the instrument cases.

- The glass bulb on a pH electrode is **very thin and quite fragile**; take care not to drop the electrode on its tip, and make sure that any stir bar being used will not bump it.

- In order to calibrate the pH meter, you will often need to know the temperature of the calibration solutions and all of the solutions you measure should be at the same temperature.

- You will need to rinse and dry the pH electrode when changing sample or calibration standard, so have a wash bottle and soft tissue at hand. Rinse electrodes with distilled water before and after measuring a sample. Blot the end of the electrode with lint-free paper to remove excess water.

  NOTE: Never wipe the electrode to remove excess water - wiping can create static charges that interfere with correct pH measurement.

- For experiments involving extended pH range measurements, use two or three different pH calibration buffers.

- Do not re-use buffer solution or you can get cross-contamination. Take a small amount of the buffer solution and transfer it to a small glass vial to do the calibration.

General Information

The pH measurement uses an electrode system consisting of a pH sensor (pH half cell), whose voltage varies proportionately to the hydrogen ion activity of the solution, and a reference electrode (reference half cell) which provides a stable and constant reference voltage. The pH electrode consists of a thin membrane of hydrogen sensitive glass blown on the end of an inert glass tube. This tube is filled with an electrolyte, and the signal is carried through Ag/AgCl wire. This is a pH half cell. A similar system, but without using a hydrogen sensitive glass, is used as a reference. A small filter (diaphragm) connects this tube to the external liquid. This system is called a reference half cell.

The meter measures the difference between the pH half cell and the reference half cell in millivolts DC. This millivolt reading is read by the unit and displayed in either mV or pH units.

Preparing to use the pH Meter

1. Remove the protective cap from the electrode.
   DO NOT BE ALARMED IF ANY SALT DEPOSITS ARE PRESENT. This is normal with electrodes and they will disappear when rinsed with water.

2. Shake the electrode down as with a glass thermometer to eliminate any air bubbles inside the electrode.

3. If the bulb and/or junction are dry, soak the tip of the electrode in a storage solution or pH 7 or pH 4 buffer for at least an hour prior to using it.

4. Remove any salt (potassium chloride) deposit that may have formed on the surface of the electrode during storage or shipping by thorough rinsing with tap water. The presence of salt deposits is normal and generally indicates that the reference junction is open and free-flowing.

5. Lower the rubber sleeve or unscrew the plug to expose the reference fill hole. This allows the reference chamber to "breathe" and quickens the electrode's response time. This does not apply to gel and solid-filled electrodes.

6. All refillable electrodes are shipped with the reference chamber filled. Once the level of the reference solution is 1/2" (1cm) below the fill hole, add more reference electrolyte with a syringe by unscrewing the plug or lowering the sleeve. Use 3.5 M KCl/AgCl reference electrolyte for single junction electrodes and 3.5 M KCl for double junction electrodes. Hold the electrode horizontally to obtain a level above the fill hole. Replace the plug or slide the cover back when finished.

7. The electrode's glass bulb should always be kept wet. If dry, the tip should be soaked in storage solution or in its absence, in pH 4 buffer for 2 hours to hydrate the pH glass membrane before use or calibration.

8. Connect the electrode to the meter.

9. Calibrate the meter using appropriate buffer solutions. (See Calibration instructions below).

10. Immerse the tip in the sample, stir gently and wait for the reading to stabilize. For a faster response and to avoid cross contamination, rinse the tip with a few drops of the solution to be tested, before taking measurements.

NOTE: To minimize clogging and ensure a quick response time, the glass bulb of the pH electrode and the junction should be kept moist. Replace protective cap with a few drops of a storage solution, or in its absence, pH 7 or pH 4 buffers. **NEVER STORE THE ELECTRODE IN DISTILLED OR DEIONIZED WATER.**

Other Helpful Comments and Hints

- If bubbles are seen in the bulb area, hold the electrode by its cap and shake downwards until bubbles are removed.

- To improve speed of response, vigorously stir the electrode in the sample, buffer, or rinse solution.

- After exposure to a sample, buffer, or rinse solution, shake the electrode with a snap motion to remove residual drops of solution.

- Use part of the next sample/buffer to be measured as a rinse solution, when possible.

- When calibrating, use a buffer as close as possible to the expected pH of the sample.

- Keep buffers and samples at the same temperature to avoid temperature effects.

- pH readings stabilize faster in some solutions than others; allow time to stabilize.

- Electrodes deteriorate over time. If accuracy falls to 10% the electrode should be cleaned or replaced. If no improvement is observed, try a different electrode to verify that is the problem.

Good Laboratory Practices

Follow the recommendations below for accurate pH measurements. pH electrodes are sensitive measuring devices and should be cared for properly.

Correct Electrode Storage

Correct electrode storage maximizes electrode performance and extends the electrode life. Do not store pH electrodes in distilled water. The filling solution will be diluted and the electrode response will be slow.

Proper Maintenance and Cleaning

Inspect the electrode weekly for scratches, cracks or salt crystallization. If the readings become slow or drifty, clean the electrode per the manufacturer's instructions. Excessive cleaning may impair electrode performance and shorten electrode life.

Electrode Fill Hole Cover

If using a refillable electrode, remove the fill hole cover during calibration and measurement to ensure a uniform flow of electrode filling solution. Cover the fill hole overnight and during storage.

Filling Solution Level

The filling solution level must be higher than the sample level to maintain a uniform flow of filling solution. At least 1 inch above sample height is recommended, and 1/4 inch below the filling hole on the electrode.

Rinsing

Rinsing prevents contamination by carry-over on the electrodes. Rinse with deionized water or an aliquot of the buffer, standard or sample. Blot rather than wipe the pH electrode glass bulb. Transfer of static charge onto the glass bulb will result in slow or drifty response.

Stirring

Stir all buffers and samples at a uniform rate to obtain a representative sample measurement and improve electrode response time. Use a magnetic stirrer at a moderate speed. Use a piece of insulating material (e.g. Styrofoam or cardboard) between the stir plate and the beaker to prevent heat transfer.

pH Buffers

pH Buffers should be accurate and free of contamination. Keep the buffer or standard bottle tightly sealed. Do not re-use buffers and standards. Verify the buffer or standard is within the expiration date before use. If trouble arises use freshly made-up buffer solution.

Temperature

To account for pH slope, buffer and sample changes, use a separate or integrated automatic temperature measurement. Calibrate at least once a day with 2 or 3 buffers that bracket the expected sample range. Choose pH buffers that are no more than 3 pH units or no less than 1 pH unit apart.

Maintenance and Storage of pH Electrodes

A regular maintenance schedule and proper storage of your pH electrode will maximize performance, help extend the life of your electrode, and avoid the cost of frequent replacements.

Conditioning

After removing the electrode from soaking bottle or protective cap at the bottom of sensor, place the electrode in a clean container containing one of the liquids i.e. 4.0 M KCl or pH 7.0 buffer. Soak electrode for 30 minutes if left dry.

> **NOTE**: Never condition the electrode in distilled water or deionised water as long term exposure to pure water will damage the special glass membrane.

After conditioning the sensor, rinse the electrode with distilled or deionised water. The electrode is ready for calibration and measurement.

Weekly Maintenance

On a weekly basis you should inspect your electrodes for scratches, cracks, salt crystal build-up, and membrane/junction deposits. The reference chamber of refillable pH electrodes should be drained, flushed with fresh filling solution and refilled. Use a dedicated pH electrode storage solution to keep your electrode in proper working order. These storage solutions are typically composed of a mixture of different salts, preventing dilution of the electrode filling solution. Constant use of this solution for storage of your electrodes will keep your electrode ready to use and provide fast, stable response to maintain the life of your electrode.

Storage

The sensor should never be stored dry. Always keep pH electrode moist. Proper pH electrode storage maximizes electrode performance and extends electrode life.

DO NOT store an electrode in distilled or deionised water - this will cause ions to leach out of the glass bulb and render your electrode useless.

Short-term Storage (between measurements/up to one week)
Soak electrode in pH storage solution (as above)

Long-term Storage (more than one week)
The reference chamber should be filled and the fill hole securely covered. Cover the sensing element and reference junction with its protective cap containing a few drops of storage solution.

Cleaning of pH Electrodes

The solution used to clean pH electrode depends on the presence of possible contaminants. Mechanically intact electrodes may show slow response due to coating or clogging.

After any of these cleaning procedures, it is good practice to thoroughly rinse the pH electrode with deionised water then drain and refill the reference chamber and soak the electrode in storage solution (or pH 7 buffer) for one hour.

General cleaning

Soak the pH electrode in 0.1 M HCl or 0.1 M HNO_3 for 20 minutes. Rinse well in tap water before use.

A second general cleaning procedure involves soaking the electrode in a 1:10 dilution of household laundry bleach in a 0.1-0.5% liquid detergent solution in hot water with vigorous stirring for 15 minutes.

Removing stubborn deposits and bacteria

Soak the pH electrode in a 1:10 dilution of household laundry bleach for 10 minutes. Rinse thoroughly before use.

Removal of grease and oil

Rinse the pH electrode in mild detergent solution or methyl alcohol. Wash in water before use.

Removal of protein deposits

Soak the pH electrode in 1% pepsin in 0.1M HCl for 5 minutes. Rinse well in water before use.

Removal of inorganic deposits

Soak the electrode in 0.1M tetrasodium EDTA solution for 15 minutes

CAUTION: Proper eyewear and hand gloves must be used when handling strong chemicals.

Troubleshooting Chart

Symptom	Cause(s)	Recommended Solution
Long response time Noisy or fluctuating reading Reading drifts	Clogged or dirty junction	Soak in 4.0 M KCl @ 60ºC for 30 minutes. Recalibrate the meter.
	Air bubble insulating the junction	Shake the electrode down as with a clinical thermometer.
	Deteriorated gel layer	Soak in 0.1 M HCl overnight.Recalibrate the meter
	Oil, paint, dyes, suspended solids on sensor	Rinse electrode alternately with materials solvent then pH 7 buffer.Recalibrate the meter.
	Protein coating on electrode surface	Soak in 1 g of pepsin dissolved in 100 mL of 0.1 m HCl for 30 minutes or as needed. Recalibrate the meter.
	Organic solvents are coating sensor	Organic mole fraction has to be less than 50% to assure reasonable readings.
	Dehydrated membrane	Limit time of measurement. Keep the electrode in pH 7.00 buffer between readings.
Dry Bulb	Long term storage without wetting.	Soak electrode tip in wetting cap filled with 1 mL 7.00 buffer for 24 to 48 hours. Recalibrate the meter.
Static Charge	Wiping electrodes	Rinse electrode in 7.0 buffer and blot. Do not wipe electrode.
Same readings in different buffers and samples	Cracked or broken bulb	Replace electrode. Use bulb guard. Avoid plunging electrode to bottom of container and spinning bars. A wetting cap will protect bulb between measurements.
Erratic LCD display	Samples have low ionic strength (lacks salt); e.g. distilled, de-ionized, boiled, lake water (high pressure)	For each 50 ml of sample add 1 drop (50 uL) of saturated aqueous solution of KCl. No alteration in pH will occur by inert KCl.

Calibrating a Fisher Accumet Model 910 pH Meter

1. Set the **Function** selector to **STANDBY**.
2. Rinse the electrodes with distilled or deionised water and dry them gently with absorbent tissue.
3. Ensure the air hole is open at the top of the electrode by turning the cover.
4. Immerse the electrodes in **pH** 7.00 buffer solution and measure the temperature of the buffer solution. Set the **SLOPE** control to 100%.
5. Set the **Function** selector to **pH** and adjust the **STANDARDIZE** control to set the reading to exactly 7.00.
6. Set the **Function** selector to **STANDBY**. Remove the electrodes from the **pH** 7.00 buffer, rinse them with distilled or deionised water, and dry gently with absorbent tissue.
7. For a one-point **calibration**, proceed to step 7. For a two-point **calibration**, immerse the electrodes in the second **calibration** buffer (**pH** 4.00 or 10.00) and set the **Function** selector to **pH**. Adjust the **SLOPE** control until the display reads the same **pH** as the second **calibration** solution. Remove and clean the electrodes as in step 5.
8. Immerse the electrodes in the sample. Set the **Function** selector to **pH** and record the **pH** reading.
9. When you have finished taking readings from a particular sample solution, set the **Function** selector to **STANDBY**.
10. Remove the electrodes, rinse and dry them gently, and close the air (filling) hole near the the top of the electrode by rotating the cover. Leave the electrode immersed in the storage solution.