pH

VT WSMD Wastewater Program Lab Manual Section #7

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pH

Background

pH is among the most important analyses performed at wastewater facilities. This is because so many processes are affected or dependent upon specific, sometimes narrow pH ranges. Important processes such as chemical coagulation, water softening, chlorination, corrosion, nitrification, BOD and many others occur efficiently only within certain pH ranges. Biological processes such as aerobic and anaerobic digestion, RBC treatment and reactions in aeration tanks are other examples of processes where operation outside of a narrow pH range can seriously reduce treatment efficiency.

The term pH is used to express how acidic or basic a material/solution is. pH is expressed as the negative logarithm of the hydrogen ion concentration. Therefore, a pH of 4 represents $1 * 10^{-4}$, or 0.0001, mol/L hydrogen ion concentration. We will explain this in more detail later in this section.

The Chemistry of pH

pH is actually a measurement of the hydrogen ions in water solution in moles/l. As previously mentioned, most common acids produce hydrogen ions (H^+) and most common bases produce hydroxyl ions (OH^-). An acid, HCL (Hydrochloric acid) for example, dissociates or breaks up to produce hydrogen ions and chlorine ions. This is written as follows:

$$HCl \rightarrow H^+ + Cl^- \quad (in\ aqueous\ solution)$$

Sulfuric acid would dissociate as follows:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-} \quad (in\ aqueous\ solutions)$$

Since these materials have the free hydrogen ions in common, they are both acids. The same type of process applies to bases. For example, sodium hydroxide (NaOH) dissociates in water to produce Hydroxyl ions (OH^-) and sodium ions (Na^+):

$$NaOH \rightarrow Na^+ + OH^- \quad (in\ aqueous\ solution)$$

Potassium hydroxide (KOH) will dissociate to produce potassium ions (K^+) and hydroxyl ions (OH^-):

$$KOH \rightarrow K^+ + OH^- \quad (in\ aqueous\ solution)$$

These materials have the free hydroxyl ions in common and are both bases.

The degree to which a material dissociates depends on the amount of hydrogen ions or hydroxyl ions present, and therefore, determines the pH of the solution. Strong acids and strong bases dissociate to a greater extent than weak acids and bases.

Water, also weakly dissociates to form hydrogen ions and hydroxyl ions:

$$H_2O \rightarrow H^+ + OH^-$$

With the development of the pH electrode, chemists were able to measure the quantity of hydrogen ions present. In perfectly pure water $H^+ = 10^{-7}$ moles per liter and $OH^- = 10^{-7}$ moles per liter. The pH scale is derived by taking the negative of the log to the base 10 of the hydrogen ion concentration. In

other words, if the hydrogen ion concentration is 10^{-7} moles per liter, the pH will be 7, being the negative log to base 10 of the hydrogen ion concentration. A solution with the hydrogen ion concentration of 10^{-13} moles per liter would have a pH of 13.

Since pH is a logarithmic function, the most important thing to realize from a practical standpoint is that each single digit increase or decrease in pH represents a ten-fold change in concentration. For example: A solution with a pH of 2 is ten times more "acidic" than a solution with a pH of 3. This pH 2 solution would be one hundred times as acidic as solution of pH 4, and one thousand times as acidic as a solution of pH 5. The lower the pH number, the more acidic with seven being neutral.

Sometimes seeing pH expressed in scientific notation, as shown below, helps the reader appreciate the relationship between pH when expressed as a whole number and the actual concentration of hydrogen ions that this number represents.

pH		**H^+ in mol/L**
1	*	10^{-1} ---------- 0.1
2	*	10^{-2} ---------- 0.01
3	*	10^{-3} ---------- 0.001
4	*	10^{-4} ---------- 0.0001
5	*	10^{-5} ---------- 0.00001
6	*	10^{-6} ---------- 0.000001
7	*	10^{-7} ---------- 0.0000001
8	*	10^{-8} ---------- 0.00000001
9	*	10^{-9} ---------- 0.000000001
10	*	10^{-10} ---------- 0.0000000001
11	*	10^{-11} ---------- 0.00000000001
12	*	10^{-12} ---------- 0.000000000001
13	*	10^{-13} ---------- 0.0000000000001
14	*	10^{-14} ---------- 0.00000000000001

Whereas we could carry out this "more acidic than" analogy up to pH 14, stating that a pH of 1 is 10 trillion times as acidic as a pH 14, in solutions with higher than pH 7 it is really the basicity of the solution ($0H^-$) ions we are concerned with. The inverse is true for basicity. In other words; regarding basicity, the larger the number the stronger the basicity. For example, a pH of 8 is 10 times more alkaline than a pH of 7.

Methods of pH Measurement

Around 1925, the glass pH electrode was developed. Although it was a very satisfactory method of pH measurement under lab conditions, the fragile and cumbersome nature of this electrode made it unsuitable for field work. It also was adversely affected by high salinity and samples containing oil and grease.Modern electrodes are used in two-electrode systems or as a single combination electrode. The combination electrode with a plastic sleeve to protect the fragile tip is preferable.

Since there are many types of pH probes on the market, be sure to follow the manufacturer's instructions for your probe carefully regarding maintenance and pre-use preparation. Reference electrodes should be checked frequently for crystals in the probe body. A small amount of crystal might not hurt the electrode's performance but electrodes that have been allowed to dry out and have crystals well up the body might have to be discarded. By draining the filling solution, putting in distilled water, waiting 30 minutes, then repeating the process of draining and refilling with distilled water, it is possible to remove the crystals. Then flush with filling solution and refill. This process is laborious and time-consuming. This can be avoided by keeping the filling hole closed between uses. It must, however, always be open when the probe is in use! The glass electrode should be checked for an excessive air bubble. Small bubbles will not interfere with performance, but bubbles which occupy a large part of the tip will interfere.

Equipment

pH meter

The required specifications for pH meters include:

1) It must have a range of 0 to 14.
2) It must be capable of two-point standardization
3) It must have a pH accuracy rating of ± .01.
4) It must have slope display/control

Recommended specifications include:

1) Automatic Temperature Compensation (ATC)
2) Digital readout
3) "Low Battery" warning for portable units.

pH Probe

There are hundreds of pH probes available on the market designed for every conceivable use. When ordering a pH probe, be sure to choose one suited for your application. Generally, gel-filled probes are less expensive than the refillable type probes, but gel-filled probes must be replaced every six months to one year. This is because there is a limited amount of electrolyte solution in the probe and when it is used up, there is no way to rejuvenate the gel. The refillable type probes, on the other hand, if well maintained, could conceivably last much longer, justifying the initial expense.

Thermometer

Even if a pH meter is equipped with Automatic Temperature Compensation (ATC), it is still a good idea to check the temperature of the sample with a thermometer as a comparison for quality control. Both the meter's temperature probe and the thermometer used to verify the temp must be compared to a

NIST traceable thermometer annually. The ATC should be checked weekly with a NIST traceable thermometer.

Absorbent Papers

Kimwipes (or comparable lab tissue) are specially designed for laboratory use and are especially good for wiping down the pH probe and gently removing liquid from the glass tip.

Wash Bottle

A wash bottle, filled with distilled water, is used to rinse the pH probe.

Beakers or Plastic Bottle

Small (50 milliliter or less) beaker or clean plastic Dissolved Oxygen bottle caps can be used for buffers for standardization buffers. The buffers should be discarded after use.

Magnetic Stirrer (with stirring bar)

This device is extremely helpful in maintaining a constant movement of the sample during analysis. A slow, constant mixing produces a good homogenous sample and improves accuracy. Be careful not to break the electrode end. Mix rate should not create a vortex.

Reagents

- Distilled water
- pH buffer 7
- pH buffer 4
- pH buffer 10
- pH buffer 7 from a different lot (or pH buffer closer to typical expected pH.)

The pH buffers can be purchased in a variety of forms, pre-made, concentrated liquid, powder, tablet, etc. Use of the pre-made buffers is highly recommended as they are very reliable, generally have a shelf life of one to two years and are available in color-coded form for easy identification. If using the powder or tablets, be sure to follow the manufacturer's instructions carefully. Buffers should be NIST traceable. Prepared buffers should be purchased in 1 Liter volumes. It is not recommended to purchase larger volumes because of contamination and/or expiration issues. The date that a buffer is opened should be recorded on the container. Buffers have a shelf-life once opened. Check with the manufacturer to know when the buffer should be discarded and replaced.

Procedure

Standardization of the Meter

The meter must be standardized before each use. This should be done before the samples are collected.

1) **Turn on meter** and allow 10 – 15 minutes for stabilization. This allows the probe to polarize, necessary for accurate pH measurement.
2) Remove electrode(s) from storage and **rinse down with distilled water** using the wash bottle. Be sure to follow manufacturer's instruction for short-term or long-term storage of electrode. Concentrate the rinse to cover the reference junction and glass tip. It may be necessary to turn the

probe upside down to thoroughly rinse the area around the glass tip and remove contamination from /around and under the protective cap carefully.

3) **Blot dry with Kimwipes,** being careful not to touch the tip of the electrode. You can use the corner of the Kimwipe to pull a drop off the tip by touching it to the drop (not the electrode).

4) **Immerse the electrode(s) in a buffer no more than one or two pH units from the expected sample pH.** pH 7 is usually a good choice to set the response point. Be sure to immerse the probe so that both the glass tip and the reference junction are submerged, turn the magnetic stirrer on low or swirl the buffer. Record the pH of the buffer after the meter stabilizes.

5) Remove the electrode from the buffer, **rinse** down with distilled water and blot dry.

6) **Immerse the electrode in a second buffer** which should be (at least) three (3) units from the first, usually pH buffer 4 or 10. If your samples are on the acid side of pH 7, use a pH 4 buffer; if on the basic side, use a pH 10 buffer. Record pH reading after the meter stabilizes.

7) **Check the value of a third buffer. The third buffer should be between the standardization buffer values.** If you calibrated with pH 4 and 7, it is recommended to check the calibration with a buffer between 4.5 – 6.5. If you calibrated with pH 7 and 10, it is recommended to check the calibration with a buffer between 7.5 – 9.5. Checking a two-point calibration with another pH 7 buffer does not test the slope of the line, and therefore the calibration, of the pH meter.

    a. If the electrode(s) and meter are operating well the value shown on the meter should be less than 0.1 pH units from the stated buffer value.

Probe Maintenance

Applying air pressure to the fill hole of the probe is a simple probe maintenance procedure that, if performed on a regular basis, can lengthen the life of your re-fillable glass probe. This can be done by putting the nozzle of the empty filling solution bottle to the fill hole and squeezing. (Pressure should be maintained for 15 seconds.) When pressure is applied there should be a slight leaking of the filling solution for the junction area. If there is no leaking of solution, the probe has a clogged junction which can result in drifting, slow response, erratic readings, etc. To alleviate this problem, follow the manufacturer's instructions for cleaning the junction. Unfortunately, this procedure cannot be used on most gel-filled probes which usually have no fill hole.

Typically, cleaning refillable type probes consists of draining the fill solution (through the fill holes), filling the probe with distilled water, and draining until all traces of crystals and contaminants are removed. Then refill the probe with the appropriate filling solution (specific for the type of probe being used).

Probe Storage

Literature suggests that it is best to store the probe in pure potassium chloride solution when not in use. Ideally this KCL solution should be the same concentration as used in the filling solution on refillable probes or the gel in gel filled probes. Storage solutions can be purchased through any scientific instrument supplier, but it might be best to purchase storage solution for the specific type of probe being used.

NEVER STORE THE PROBE IN DISTILLED WATER!! This will damage the electrode by leaching ions from the glass membrane and reference electrode.

At the end of this section is a pH probe maintenance guide graciously supplied by the Hanna Instruments Company for your use. Although the information is somewhat specific to Hanna pH probes, much of it is excellent information that can be applied to most pH probe brands. **For specific information regarding the probe you are using, be sure to consult the user's manual for your specific probe.**

Sampling

pH samples have very short hold times and are subject to changes due to gases exchanging between the sample and the atmosphere. For this reason, the grab sample collected for pH analysis must be taken after the pH meter is standardized and then analyzed immediately. To prevent the exchange of gases the sample should be collected without agitation into a DO bottle, filled to the neck, and tightly stoppered. Samples MUST be analyzed within 15 minutes. The sooner the better! Alternatively, using a standardized meter, perform the analysis by placing the probe directly into the waste stream. There is no preservation method for pH samples.

Analysis

After meter standardization:

1) Raise the electrode(s) from the storage beakers, rinse down thoroughly with distilled water, and blot dry.
2) Be sure to include the glass bulb the area around it, the reference junction(s) and the probe body in the rinse.
3) Be sure to have the temperature probe in the sample.
4) Allow the meter time to equilibrate (to reach stable reading).
5) Record the pH and temperature at time of sample analysis.

pH values should be recorded to the nearest 0.1 pH units at the temperature of the sample. For example: pH= 7.3 at 21°C. This is because the temperature affects pH readings in two ways. Electrodes are sensitive to temperature changes and the potential, or voltage, they generate in response to the pH of solution changes with temperature. The potential pH unit change is accounted for by using a meter with temperature compensation. The second way in which temperature affects pH reading is that the ionization in the sample changes with temperature. This change is inherent in the sample and cannot be accounted for by the meter. It is important, therefore, to report the temperature at which the pH of the sample was read and analyze as soon as possible after sample collection. (Maximum hold time = 15 minutes).

Quality Control

Along with good sampling, the best method of assuring good quality data is the careful standardization of pH meters to two (2) buffers with a check of the third buffer to establish linearity. Standardization to

one (1) buffer is not sufficient. A malfunctioning pH meter or electrode may still read seven (7) but will not be able to accurately read pH 4 or pH 10.

Take a duplicate pH sample (in other words, collect samples in two (2) bottles at one of your sampling stations) at least once per week to be sure that the data is reproducible.

Most problems with pH analysis involve the pH probe, not the meter. A simple method to determine if the meter is malfunctioning is: Straighten a paperclip, place the end of the paperclip into the hole in the center of the BNC connector on the meter, then bend the paperclip to make contact with the metal ring of the BNC connector (see photo). The meter should display a reading of 7.00 +/- 0.1. (6.9-7.1). If it does not, there may indeed be a problem with the meter. If you are not comfortable with doing this yourself, contact the manufacturer to troubleshoot issues you are having.

A minimum 10% duplicate/replicate schedule must be established for the pH analysis; therefore, a duplicate/replicate analysis must be performed once every 10 pH analyses. Most operators choose to establish a once per week duplication/replication schedule.

Here is a link to the Hanna® pH meter and method. Be sure to use the instructions supplied with the meter in use at your facility. There are often subtle differences between brands. This link gives good information on use/care, calibration, and maintenance requirements for model 991001 portable pH meter.

MAN991001_12_18.pdf (hannainst.com)