pH

pH

Background

The term pH is used to express how acidic or basic a material is. Although we generally think of pH as being run on solutions, pH is also done on soils, agar gels, and other materials. The pH scale runs from pH 0 to pH 14, with the neutral point being pH 7. **Acidic** solutions range from pH 7 down to pH 0; the lower the pH, the more acidic is the solution. **Basic** solutions range from pH 7 up to pH 14; the higher the pH, the more basic the solution.

The pH of most natural waters is between pH 4 and pH 9. Some being slightly basic because of a carbonate buffer system, which tends to pick up some of the hydrogen ions in solution. But many natural waters are becoming slightly to moderately acidic due to a variety of factors, including "acid rain".

The pH of water is important because it affects such things as chemical coagulation, water softening, chlorination, and the corrosivity of water. pH also affects biological processes such as anaerobic and aerobic digesters, biological reactors such as aeration tanks and RBCs, and the biological processes in streams. The organisms responsible for treatment in these biological processes have a somewhat narrow range of pH tolerance, outside this range treatment efficiency is greatly reduced. It is important that the operator know the pH in the process especially the biological processes, especially if the treatment plant is receiving industrial wastes.

The Chemistry Of pH

pH is actually a measurement of the hydrogen ions in water solution in moles/l. 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, in this case, chlorine ions. This is written as follows:

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

Sulfuric acid would dissociate as follows:

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

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

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

$$KOH \qquad K^+ + OH^- \text{ (in aqueous solution)}$$

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

The degree to which a material dissociates determines 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, too, weakly dissociates to form hydrogen ions and hydroxyl ions:

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

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 7.7, being the negative log to base 10 of the hydrogen ion concentration. A solution with the hydrogen ion concentration of 10^{-13} moles/l 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 ~~basic,~~ with seven being neutral.
acidic

Sometimes seeing pH expressed in scientific notation, as done 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 (whole number representation)			Hydrogen ion concentration (in moles per liter)	
pH 1	1	*	10^{-1}	0.1
pH 2	1	*	10^{-2}	0.01
pH 3	1	*	10^{-3}	0.001
pH 4	1	*	10^{-4}	0.0001
pH 5	1	*	10^{-5}	0.00001
pH 6	1	*	10^{-6}	0.000001
pH 7	1	*	10^{-7}	0.0000001
pH 8	1	*	10^{-8}	0.00000001
pH 9	1	*	10^{-9}	0.000000001
pH 10	1	*	10^{-10}	0.0000000001
pH 11	1	*	10^{-11}	0.00000000001
pH 12	1	*	10^{-12}	0.000000000001
pH 13	1	*	10^{-13}	0.0000000000001
pH 14	1	*	10^{-14}	0.00000000000001

Methods Of pH Measurement

About 1925, the glass pH electrode was developed. Although it was a very satisfactory method of pH measurement under lab conditions, the fragile 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.

For field work some other methods involving indicator solutions, were developed. Indicator solutions would turn a specific color when added to solutions of a specific pH. These colors were calibrated against the hydrogen electrode. In practice, the indicator is added to the sample, mixed, and its color compared to a chart listing the colors and pHs. This method is relatively inexpensive but it is reliable only between pH 3 and pH 10. There are interferences from turbidity, color in the sample itself, various oxidants, and reductants present in the sample may change the indicator color. The indicator itself may change the sample pH and finally indicators, color charts, and standards will deteriorate with time.

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.

Most brands of new electrodes should be soaked in distilled water overnight before use. 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 crystals 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. You would then flush with filling solution and refill. This process is laborious and time-consuming; avoid it 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 control.

Recommended specifications include:

1) Automatic Temperature Compensation
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 due to the fact that 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 forever, justifying the initial expense.

Thermometer

Even if your pH meter is equipped with Automatic Temperature Compensation, 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.

Absorbent Papers

"Kimwipes" 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

Fifty (50) to one hundred (100) milliliter beakers are used for buffer storage as well as for sample containment during the analysis.

Magnetic Stirrer (with stirring bar)

This device is extremely helpful in maintaining a constant movement of the sample during analysis.

Reagents

Distilled water
pH buffer 7
pH buffer 4
pH buffer 10

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.

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 30 minutes for stabilization (15 minutes for most newer meters).

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.

3) **Blot dry with Kimwipes,** being careful not to touch the tip of the electrode. The glass tips scratch easily and any scratches greatly damage 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). Be very careful.

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. Set the temperature compensation knob to the buffer temperature. **Adjust** the meter, using the standardization knob, to read the buffer value while the solution is stirred or agitated. Pay careful attention to the buffer temperature and the stated pH value of the buffer at the temperature.

5) Remove the electrode(s) from the buffer, **rinse** down 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. **Adjust** the meter to read the correct buffer value using the slope control.

7) **Check the value of a third buffer** (on the opposite end of the pH scale from the second buffer). 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

There is a very simple probe maintenance procedure that, if performed on a regular basis, can lengthen the life of your glass probe indefinitely. That is, apply air pressure to the fill hole of the 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 from the junction area. If there is no leaking of solution, your 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.

Sampling

As stated in the section on sampling, pH samples have no holding time and are subject to changes due to gases exchanging between the sample and the atmosphere. For this reason, the sample must be taken after the meter is standardized and then analyzed immediately. To prevent the exchange of gases, take the sample without agitation into a DO bottle, fill to the neck and tightly stopper.

Alternatively, using a calibrated portable meter, perform the analysis by placing the probe directly into the waste stream. There is no preservation method for pH samples.

Analysis

1) Raise the electrode(s) from the storage beakers, rinse down thoroughly with distilled water, and blot dry.

2) Immerse the electrode(s) in the sample and turn on the stirrer or slowly swirl the beaker.

3) Read the sample temperature and set on temperature compensation knob.

4) Allow the meter time to equilibrate (to come to a constant reading).

5) Record the pH of the sample.

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. This potential/pH unit change is accounted for by setting the temperature compensation knob. The second way in which temperature affects pH readings is that the ionization in the sample changes with temperature. As the temperature rises, more ionization occurs, thus changing the pH. 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.

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 a 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.

You should daily, take a duplicate pH sample, that is, two (2) bottles at one of your sampling stations, to be sure that the data is reproducible.

pH
TROUBLESHOOTING GUIDE

PROBLEM	MOST PROBABLE CAUSE	SOLUTION
Extreme, erratic pH readings	The probe junction may be clogged	Apply air pressure to the filling hole to check for clog Follow manufacturer's instructions for junction cleaning
	The fill hole has been left open allowing the filling solution to crystallize	Drain, rinse and refill the probe with potassium chloride solution
	Probe has exceeded it's useful life (gel filled type)	Replace probe
	Glass tip is broken	Replace probe
	Probe to meter connection not correct	Check the connection to insure both proper placement of the connector and tightness of the connection
Drifting	Electrode coated with oil and grease	Follow the manufacturer's instructions for probe cleaning (usually soaking in dilute HC1 solution will work).
	Probe junction partially clogged	Follow manufacturer's instructions for cleaning junction.
	Electrolyte needs rejuvenation	Drain, rinse and refill probe chamber with fresh potassium chloride solution.
Meter constantly displays reading of 7 or just flashes	No/low power	Check power connection or battery. Check for corrosion of battery terminals.
	Improper probe connection	Check for proper connection and corrosion of the connectors. Clean if necessary.
Meter reading no consistent with stated buffer pH	Contaminated or outdated pH buffers	Discard and replace with fresh buffers

Quality Control for
pH - Standard Methoa #4500-H

Document

Sample Collection

Grab - Exact time collected
Exact time analyzed
Location

Glassware Preparation - (+Sampling Container)

Thoroughly rinse with distilled H_2O

Equipment

Meter
- Range 0-14
- Accuracy - 0.1 pH
- Repeatability - 0.1 pH
- Temperature Compensation
- Capable of 2 Point Calibration

Calibration
- Buffers used
- Results
- Service & maintenance records

pH Probe
- Document Age & Maintenance
- (Gel filled - refillable)
- Storage & Use Instruction
- Stress Rinsing

Temperature Probe
- Must Be Connected To Meter and In Analyte During Analysis
- Calibration of Probe Against NIST Traceable Thermometer

Duplication Schedule - minimum of once per 10 analyses

REPORTING pH RESULTS
(Electrode Method)

pH (Electrode Method) Bench Sheet
ANALYST:
SAMPLE TIME and DATE:
SAMPLE LOCATION:
ANALYSIS TIME and DATE:
SAMPLE VOLUME (method):
SAMPLE TEMPERATURE:
METER CALIBRATION METHOD: (buffers used - results)
RESULT:
DUPLICATE RESULT:

References

Standard Methods for the Examination of Water and Wastewater, 18th Edition, 4500-H^+B, pages 4-65 through 4-69.