

pH Analysis

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Out of all the analytical measurements taken throughout every branch of science and process control, pH analyses are probably the most common. In the wastewater field pH analyses are important for neutralization, corrosion control, precipitation, coagulation, and biological treatment.

The term “pH” stands for the **p**ower of **H**ydrogen and is the measurement of the hydrogen ion activity in a solution. The hydrogen ion concentration (unlike other ions – Cl^- , Na^+ , Cu^{++} , for example) is very difficult to measure directly. Instead, its activity is measured indirectly by the use of specific electrodes in the solution. These electrodes are conveniently put together to make our pH probes. The electrical potential between these two electrodes in a sample is measured, and by comparing this with the potentials of known pH samples (buffers) we can approximate the hydrogen ion activity of the solution.

pH is measured on a scale of 0 to 14 with the lower values indicating high hydrogen ion activity (more acidic) and high values indicating low hydrogen ion activity (less acidic). A pH of 7 at 25 C is neutral. Every whole unit of pH change represents a ten-fold change in the hydrogen ion activity. For example, a pH of 5 is ten times more active than a pH of 6 and a pH of 4 is one hundred times more active than a pH of 6.

As with any analytical test, you want to make sure your results are accurate and precise. You don't want to hold an industrial user in noncompliance based on erroneous pH values. Neither do you want to be in violation with your NPDES permit based on inaccurate pH values. Erroneous results can happen because of improper calibration, instrument drift, lack of temperature compensation, improper sampling, or a dirty probe.

At the start of every shift the pH meter must be calibrated. If pH measurements are not done that often, then calibrate before every analysis. Calibration should be done using at least two buffers that bracket the sample being tested. While the most common buffers for calibration are 4, 7, and 10, use ones that will cover the range of your samples. The rule of thumb is that buffers should be within two pH units of the sample. During use, always remove the fill hole cover on refillable electrodes. This helps to keep the internal solution flowing uniformly through the glass membrane. Record all calibration data (buffers used, temperature of buffers, meter calibration settings, date/time, technician, etc.) in a permanently bound notebook.

Samples for pH should be grab samples and must be tested immediately. If samples cannot be measured directly in the field, they must be measured within 15 minutes of collection. Sample containers can be either glass or plastic. Make sure there is no headspace in the container because some samples not at equilibrium with the air can change pH within a very short time. (Note: atmospheric carbon dioxide can have a large impact on pH. For example, in the distilling process, water is evaporated then condensed

to remove most of the impurities. During this process, the carbon dioxide in the air dissolves in the water to form carbonic acid. Under ideal conditions, this gives distilled water a pH of 5.65, not 7.0 as many believe. Coincidentally, our natural water cycle of evaporation, cloud formation, and rain works in a similar way. That is why acid rain is defined as having a pH of less than 5.65)

Always rinse the end of the pH probe and blot dry before putting it into a solution. Gently mix the solution with a magnetic stirrer being careful not to cause a lot of surface disturbance. Make sure the temperature of the sample is the same as the buffers used to calibrate if your meter does not have temperature compensation abilities. Always record initials of person performing the test, date/time, location, temperature of the solution, and the pH in a bound notebook.

In most situations, pH probes are relatively free from interference. However, all suffer from accumulated “dirt” on the glass bulb at the tip of the probe. The bulb is a glass membrane that allows certain ions in solution pass through. If the probe is responding slowly then there may be material (grease, protein, and other debris) that is blocking the flow of these ions and will need to be removed. Follow the manufacturer’s direction for cleaning solutions and times.

The pH probe should be stored wet when not in use. The type of storage solution will depend upon the recommendations of the manufacturer and the type of pH probe. However, in almost all cases a buffer or salt solution is used. Do not use distilled or deionized water as this may dilute the probe’s internal solution.

The recommendations in this article for testing and recording pH analyses are very general. Always check your state and local regulations. You may have additional requirements to meet.

References:

Standard Methods for the Examination of Water and Wastewater, 24th ed. 2023. Part 4500-H⁺ pH Value.

Standard Methods for the Examination of Water and Wastewater, 24th ed. 2023, Table 4020: I Minimum Quality Control Measures in Part 4000 (footnotes 2,5,9).

Title 40 Code of Federal Regulations, § 136, Table II

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