pH Essentials Guide

Practical Description of How to Measure pH

Laboratory Environment

Essential Knowledge of pH

to Measure Correctly From the Start

METTLER TOLEDO

Content

Introduction

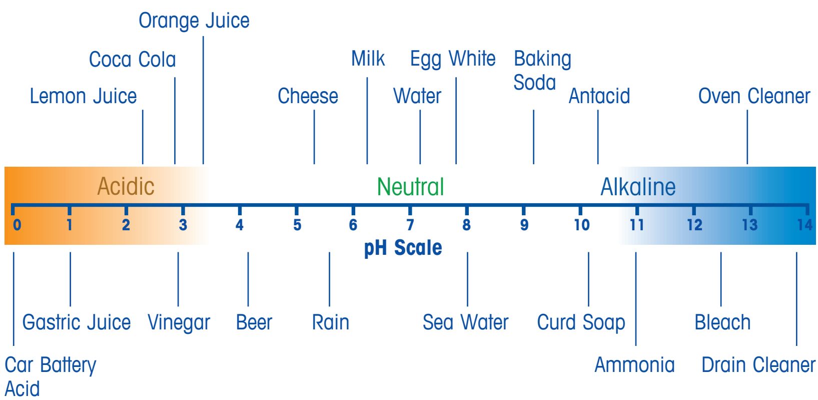
This guide is intended as a first introduction to the practice of pH measurements. The basic knowledge that is needed to understand a pH measurement is given. The tools necessary for pH measurements are explained and a step-by-step guide to perform pH measurements is provided. Finally, some practical tips & hints are given, as well as a troubleshooting guide for pH measurements.

1. What is pH?

Probably you have already heard the word pH or the terms acidic or alkaline. But, what is pH exactly? And why do we classify an everyday liquid like vinegar as being acidic?

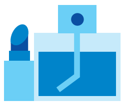
pH is a chemical property of an aqueous solution, which indicates its degree of acidity or alkalinity. pH values can vary from 0 to 14, where pH values from 0 to 7 are called acidic and pH values from 7 to 14 are termed alkaline, while a pH value of 7 is neutral.

The quantitative difference between acidic and alkaline substances can be determined by performing pH value measurements. A few examples of pH values of everyday substances and chemicals are given in the following figure:



2. Where and Why is pH Measured?

pH measurement is a widely applied analytical technique in various fields. These examples describe the importance of pH in an extensive range of applications, demonstrating why it is so often determined:

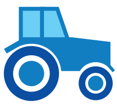


Cosmetics
During production, pH is measured to monitor chemical reactions, which define the product's consistency and suitability for the skin.

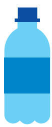
Pharmaceutical industry
In strongly regulated markets, like the pharmaceutical industry, pH is measured during production to verify the quality and compliance with safety standards.

Food and beverage
Properties such taste or appearance depend on the pH value. Therefore, pH needs to be monitored several times during the production process.

Electroplating industry
pH needs to be measured often in the electroplating industry in order to verify the status of the galvanic bath.

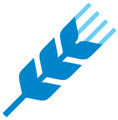


Agriculture
In case the yield of a certain production process is higher at a given pH, then the costs of production are lower at this pH. Therefore, pH measurements are essential.



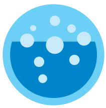
Chemicals
The measurement of pH is necessary in the plastics' manufacturing process in order to control chemical reactions such as polymerization.

Furthermore, pH can be verified in different steps of the same process. For instance, the pH values at different stages of beer brewing will have a direct effect on the quality and taste of the beer:



1. Wheat fields
The pH of the soil influences which nutrients are available to plants. If the soil's pH is above or below a given range, nutrients may not be accessible.

2. Water used
Depending on the type of malt to be processed, water with higher or lower hardness (mineral content in the water) will be needed. Therefore, it is very important to know the hardness of the water that is used, in order to reach a suitable pH level for maceration.



3. Fermentation
The pH value has an effect on the activity of the enzymes during fermentation. Measuring pH during fermentation can identify a problem in the process.

4. Final product
Last but not least, pH is also measured during the quality controls of the final product, verifying its quality.

3. Types of pH Measurement

There are mainly two systems to measure pH: pH indicators and pH meters. However, not all of them provide the same accuracy and quality level. A comparison between two widely used methods is shown below:

pH indicators
Paper or soluble compounds that change color according to pH.

- Well-established analytical technique
- Very fast
- Extremely simple to use
- A high accuracy cannot be expected (error ≥ 0.5 pH)
- Recommended for low budgets
- Difficulty to determine the exact tone of color
- Cannot be used in colored samples

pH meter and electrode
Electrochemical determination of pH value by a pH sensitive glass membrane.

- Well-established analytical technique
- Fast
- Simple operation, easy to learn
- High precision, repeatability and accuracy (error ≥ 0.05 pH)
- More expensive than pH indicators
- pH value is clearly given on the screen (no room for interpretation)
- Can be used in clear and colored samples

4. Essentials for a pH Measurement

The tools necessary for pH measurements are relatively uncomplicated and provide reliable measurements when used correctly:

1. pH electrode
A pH electrode, which typically is a combination of a glass electrode and a reference electrode, is immersed into the sample to measure its pH. The right pH electrode should be used for every application.

2. pH buffers
Before measuring pH, two or more reference solutions of known pH values must be used for the calibration of the pH electrode.

3. Sample
This is the solution to be measured, which needs to be an aqueous solution or to contain enough water for the pH measurement to be possible.

4. pH meter
The pH meter is a potentiometer that measures the voltage difference between the glass electrode and the reference electrode, and calculates the pH value.

pH electrodes have a very important role in providing correct pH readings, since they are responsible for the actual pH measurement. The variety of pH electrodes is as diverse as the applications they are used for. Only the right combination of junction, electrolyte, shape and type of the membrane glass, and shaft material, make an electrode perfectly suited for a specific application. A pH electrode consists of the following parts:

1. SafeLock™
For refillable sensors only: prevents evaporation and leakage during storage and transportation. It must be opened during measurements.

2. Shaft Material
The sensor's robustness is dependent on the right shaft material. Glass is highly resistant to chemicals and allows measurements at high temperatures. When mechanical robustness is key, plastic is the preferred material.

3. Reference Electrolyte
Sensors with a liquid electrolyte provide fast results. The ones with a polymer or gel electrolyte are not refillable and hence low maintenance.

4. Reference System
Provides a stable potential with which a measured pH potential can be compared.

5. Junctions
The junction is the connection between the reference electrolyte and the sample.

- **Ceramic Junctions** - For general applications.
- **Sleeve Junctions** - For fast results, best in dirty samples.
- **Open Junctions** - For easy handling in general applications.

6. Membrane Glass
The membrane is the pH sensing part of the sensor. Its shape and glass composition are optimized to ensure best results in different applications.

7. Temperature Probe
The pH value of a solution is temperature-dependent. Thus, the temperature should be measured with every pH value. The temperature probe is either integrated in the pH electrode or an external one can be used.

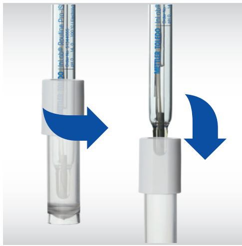
8. Wetting Cap
To keep the glass membrane hydrated. Sensors should always be stored in aqueous and ion-rich solutions.

5. Step-By-Step Guide to pH Measurements

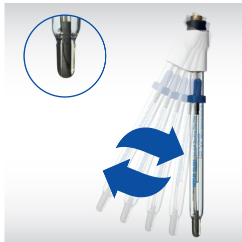
The accuracy of a pH measurement is influenced by different factors, such as the accuracy of the buffers used for calibration, whether or not temperature compensation is used, and if the right electrode is used for a particular application, to mention just a few. When great care is taken with the measurements, an accuracy of ± 0.05 pH units could be achieved. This step-by-step guide assumes that a combination pH electrode (measuring and reference electrodes in one) is used. If separate measuring and reference pH electrodes are used, ensure that you always put the electrodes in the same solution during the measurements. Also ensure that both electrodes are connected to the pH meter.

5.1. Electrode preparation

1. Connect the pH electrode and temperature probe to the pH meter.



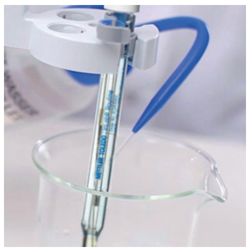
2. Remove the wetting cap from the pH electrode.



3. Check the tip of the electrode for air bubbles. If found, shake the electrode like a thermometer.

4. For refillable electrodes only: open the refilling hole before use.

5. For refillable electrodes only: check the electrolyte level (artificially colored green for illustration purposes) and refill if necessary.

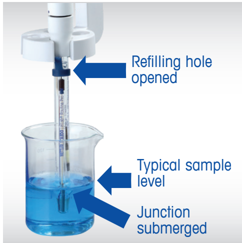


6. Rinse the electrode with distilled or deionized water.

7. The electrode is ready to perform a calibration or a measurement.

5.2. Electrode calibration

1. Select the correct buffer group or buffer values for the calibration in the meter's settings.

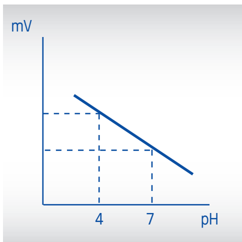


2. Pour enough pH calibration buffer into a measuring beaker and dip the pH electrode into the first buffer.

3. Press the calibration button on the pH meter and wait until the measurement is stable.

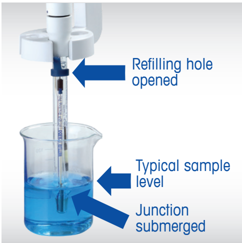
4. Take the electrode out of the solution and rinse it with distilled or deionized water.

5. Repeat steps 2–4 for each calibration buffer used.



6. Review the calibration results on the meter and save them if they are acceptable.

5.3. Measurement



1. Pour enough sample solution into a measuring beaker and dip the pH electrode into the sample.

2. Press the measurement button on the pH meter and wait until a stable endpoint has been reached.

3. Take the electrode out of the solution and rinse it with distilled or deionized water.*

4. For additional samples repeat steps 1–3 until all samples have been measured.

*In case rinsing with distilled water in step 3 is not sufficient, perform the following procedure:

1. Rinse the electrode with ethanol or acetone (for additional information, visit www.mt.com/electrode-guide -> pH TroubleShooter) until all contamination is removed.

2. Rinse again with deionized water.

3. Condition the electrode by dipping it in an electrolyte solution for several minutes.

4. Calibrate after every cleaning step with an organic solvent.

5.4. Electrode storage

For short term storage

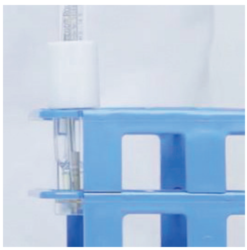
1. Place the electrode in a beaker with reference electrolyte solution or pH buffers 7.00 or 4.01.

For long term storage

1. Close the refilling hole.

2. Fill the wetting cap with the appropriate electrolyte.

3. Put the wetting cap on the electrode. Make sure that the whole membrane is covered with electrolyte solution.



4. Store the electrode vertically, membrane down.

6. Good pH Measurement Practices

Measuring pH is generally considered an easy, fast, and simple process, but so many things can go wrong. Different measurement and maintenance practices are essential to ensure the reliability and quality of pH measurements:

1. Select the correct electrode for your sample
pH electrodes play a very important role in performing correct pH value determinations, since they are responsible for the actual pH measurement. Based on your application, select the most suitable electrode.

2. Use the correct calibration buffers
The buffers used for calibration must be selected according to the sample's pH. For instance, if a sample is expected to have a pH of 7.45, the calibration must include pH buffers 7.00 and 9.21 (or similar). Use a minimum of two fresh buffers for calibration.

3. Rinse, but do not wipe the electrode
After rising the electrode with distilled water to remove salt deposits or any contamination, dab it dry with a tissue, but never wipe it. The rough surface of the paper tissue can scratch the pH-sensitive glass membrane, and/or it can create an electrostatic charge that might cause the measured signal to become very unstable.

4. Check your calibration results
The electrode calibration provides valuable data on the electrode condition. The slope of the calibration curve should lie between 95% and 102% of the theoretical value. Another measure of a good calibration is the offset at the zero point (0 mV at pH 7), which should remain relatively stable and should not exceed ±30 mV.

5. Stir the sample
When measuring pH, gently stir the sample to ensure that it is homogeneous. It is important that calibration and measurement are done under the same conditions. Do not use the electrode to stir.

6. Calibrate your pH electrode daily
Regular calibrations will lead to more accurate results. Some applications might require a calibration before every measurement, but in general it is enough to calibrate every 24 hours.

7. Measure the temperature of the sample

Every sample has a different pH behavior depending on the temperature, therefore the temperature should be measured. The temperature probe is either integrated in the pH electrode or an external one can be used. If the electrode and the sample have different temperatures, give the system enough time to equilibrate. To compare the pH of different samples, they should always be measured at the same temperature.

8. Use fresh buffers for calibration

Check the expiry date of the calibration buffers before use. Never calibrate the sensor directly in the bottle. Do not re-use calibration buffers and never pour them back in the bottle. Close the bottles immediately after use and store them at room temperature.

9. Keep the electrode cleaned

Using a dirty electrode is one of the typical sources of error in pH measurement. Make sure that the electrode is always clean and well maintained.

10. Store the electrode in a proper solution

Electrodes should always be stored in aqueous and ion-rich solutions. The electrode should never be stored dry or in distilled water as this will affect the pH-sensitive glass membrane and thus shorten the lifetime of the electrode. If not sure which storage solution to use, check the electrode's manual.

7. Troubleshooting Guide for pH Measurements

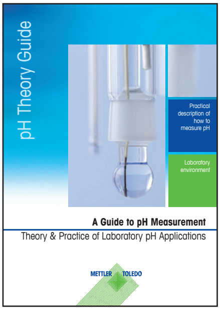
Problems that arise during pH measurements can have different sources; from the meter, cable and electrode, down to the solutions. Notes of the failure symptoms should be taken, as these are useful for locating the origin of the problem. The following table gives an overview of symptoms and causes:

Issue	Possible cause
a) No display or off-scale readings "---"	1,2,3
b) Value does not change	2,4
c) Slow response time	4,5
d) High offset or low slope after calibration	4,6,7
e) Drifting measurement values	4,5
f) Readings too high/low or out of range	4,5,8,9

Possible Cause	Cause	Possible solution
1	Power supply broken or not connected correctly	Check connections or try another power supply
2	Cable not connected to the meter or to the sensor, or defective cable	Check connections or try a different cable. Use a pH simulator
3	Low battery	Exchange battery
4	Electrode broken or in poor condition	Check the pH electrode (check electrolyte, junction, pH membrane or the age of the electrode)
5	Electrode not suitable for the application	Select the proper electrode for that application
6	Buffers used are in poor condition	Use fresh buffers
7	The set of buffers used is different from the one selected in the meter's settings	Check that you are using the right set of buffers. If not, change settings
8	Temperature of electrode and sample differs	Give the system enough time to equilibrate the temperature
9	Calibration procedure was not performed correctly	Use a minimum of two fresh buffers for calibration.

8. For More Information

The pH Essentials guide provides the basic knowledge that is needed to understand and execute a pH measurement. For more comprehensive information on all the topics mentioned in this guide, it is recommended to read the pH Theory Guide.



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- How to calibrate pH
- Temperature effects in pH measurements
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7. Glossary

pH	Chemical property of an aqueous solution, which indicates its degree of acidity (pH values from 0 to 7) or alkalinity (pH values from 7 to 14). A pH value of 7 is considered neutral.
pH meter	Potentiometer that measures the voltage difference between the glass electrode and the reference electrode, and calculates the pH value.
pH electrode (also known as pH sensor or probe)	pH electrodes are responsible for the actual pH measurement, and it is therefore crucial to use the right pH electrode for each application. In general assumed to be a combined electrode (a glass electrode and a reference electrode in one), which is immersed in the sample.
Measuring or glass electrode	It is the part that actually senses the pH of the solution. It consists of a glass shaft with a thin glass sensitive membrane at the tip. It can be combined with the reference electrode in just one electrode (combined pH electrode).
Reference electrode	It is the part that provides a defined stable reference potential for the pH sensor potential to be set against. It can be combined with the measuring electrode in just one electrode (combined pH electrode).
Junction (also known as diaphragm)	It is the connection between the reference electrolyte and the sample. It can have several different shapes and properties, depending on the application the electrode is aimed for.
Reference electrolyte	Solution that defines the potential of the reference electrode system. Which type of reference electrolyte is used in an electrode strongly depends on the reference system and the application.
Glass membrane	The glass membrane is the pH sensing part of the sensor. Its shape and glass composition are optimized to ensure best results in specific applications.
Buffer solutions or calibration standards	Standard solutions of known pH used to calibrate the pH electrodes and to check their performance.
Calibration	pH measurements in calibration standards, which establish the difference between what should be measured and what a pH electrode actually measures. It is followed by an adjustment to compensate for any deviations from the theoretical values. The term electrode "calibration" is typically used for both steps.
Sample	Solution to be measured. It needs to be an aqueous solution or to contain enough water for the pH measurement to be possible.

www.mt.com/pH

For more information

METTLER TOLEDO Group
Im Langacher 44
8606 Greifensee

30472735
Group MarCom 2480 JM