



A Review on pH and its Applications

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Abstract

The negative logarithm of the hydrogen ion concentration in a solution is known as pH, and it serves as a useful indicator of hydrogen power. The concentration of hydrogen ions is measured using a pH electrode, which determines it. One of the most basic concepts in chemistry is pH, but it also has wide applications in many other fields, including biochemistry, biology, physics, medicine, agriculture, and environmental pollution. It is particularly significant in the chemical industry, food production, environmental protection, and so on. Maintaining the pH level is crucial in quality control laboratories, as it directly influences the preparation of samples and reagents for analytical procedures. Even minor deviations in pH can significantly affect the precision and accuracy of the results after studying the different Pharmacopoeia and other literature in Scopus and PubMed-like search engines. This article thoroughly discusses the fundamental criteria for a critical instrument used in all analytical procedures, offering a detailed overview of other quantity-related necessities in analysis. This article also focuses on the applications of pH measurements.

Keywords: pH; Electrode; Calibration; Buffer Solution; pH Indicators

Introduction

The pH value measures the acidity or alkalinity of a solution. In the context of Pharmacopoeia, specific standards and limits for pH are established for substances where pH is essential for stability or physiological suitability. The pH is determined at $25^\circ \pm 2^\circ$ unless otherwise stated in the individual monograph [1].

For compendial purposes, pH is defined as the value obtained using an adequately calibrated potentiometric sensor and measuring system, traditionally known as a "pH meter". However, modern measuring systems can embed the pH sensor and transmit the pH signal digitally to external devices such as computers, Programmable Logic Controllers (PLCs), Distributed Control Systems (DCS), data acquisition systems, terminals, or other microprocessor-controlled devices.

By definition, pH is equal to $-\log_{10}[a^+]$, where a^+ represents the activity of the hydrogen (H^+) or hydronium ion (H_3O^+), and the hydrogen ion activity closely approximates the hydrogen ion concentration.

The practical pH scale is defined as:

$$pH = pHS + [(E - ES)/k]$$

E = measured potential where the galvanic cell contains the solution under test (pH)

ES = measured potential where the galvanic cell contains the appropriate buffer solution for calibration (pHS)

k = change in potential/unit change in pH and is derived from the Nernst equation (as follows)

$$k = \log_e(10) \times (RT/nF)$$

$$R = 8.314 \text{ J/mole/}^\circ\text{K}$$

$$T = \text{temperature (}^\circ\text{K)}$$

$$n = \text{moles/half-reaction}$$

$$F = \text{Faraday constant, } 96485 \text{ C/mole}$$

The resulting equation is $[0.05916 + 0.0001984(T - 25^\circ)]$ volts at temperature T. Values of k from 15°–35° are provided in Table 1.

Table 1: Values of k for Various Temperatures.

Temp.	k (V)
15.00	0.05718
20.00	0.05817
25.00	0.05916
30.00	0.06016
35.00	0.06115

The equation above can be used to determine values of k at other temperatures. For practical purposes, k values are determined from pH sensor calibration.

Approximate pH of solutions

Determine the approximate pH using a pH indicator strip R. Alternatively, pH indicators such as those described in the table below can be used.

Table 2: pH of Solutions.

Reaction	pH	Indicator
Alkaline	> 8	Red litmus paper R
Slightly Alkaline	8 - 10	Phenolphthalein solution R Thymol blue solution R
Strongly Alkaline	> 10	Phenolphthalein paper R Thymol blue solution R
Neutral	6 - 8	Methyl red Solution R Phenol red solution R
Acid	< 6	Methyl red Solution R Bromothymol blue solution R1
Slightly Acid	4 - 6	Methyl red Solution R Bromocresol green solution R
Strongly Acid	< 4	Congo red paper R

pH

A potentiometric method with a glass electrode, a reference electrode, and a pH meter, which can be either digital or analogue, can be used to determine the pH value of a solution. When operating the pH meter, follow the instructions provided by the manufacturer. Begin by calibrating the apparatus using buffer solution D as the primary standard, adjusting the meter to display the appropriate pH value based on the temperature of the solution. To set the scale, use a second reference buffer solution like buffer solution A, buffer solution E, or buffer solution G, and perform a check with a third buffer solution of intermediate pH. When measuring the electrodes, ensure that the pH reading of the intermediate solution does not differ by more than 0.05 units or at least 0.003 volts from the corresponding value indicated in Table 2. The pH measurement system requires three main components to measure pH levels accurately. First, there is a measuring electrode, typically a glass electrode sensitive to hydrogen-ion activity, although other types of electrodes are also possible. Second, there is a reference electrode, such as a silver-silver chloride electrode. Finally, there is a voltage measurement system with an input resistance capable of measuring the pH sensor’s high input impedance. These components can be configured in different ways. The measuring and reference electrodes can be separated or combined, and the voltage measurement system can be separated from or integrated into the pH sensor. Additionally, a temperature measurement is necessary to account for the Influence of temperature on pH measurements. This can be achieved using a built-in temperature sensor within the pH sensor or an external temperature measurement device. Overall, the pH measurement system is crucial for determining acidity or alkalinity levels in a given substance and requires careful calibration and maintenance to ensure accurate results [1,2].

Requirements

The pH measurement system must be able to perform a two-point or more pH calibration. The accuracy of the pH measurement system is detailed in the Calibration section. The pH measurement system should have a resolution of at least 0.01 pH. The instrument must be able to temperature-compensate the pH sensor measurement to convert the millivolt signal to pH units at any temperature. This can be achieved either automatically using a built-in temperature device in the sensor system or manually entering the sample temperature into the measurement system. The accuracy of the temperature measurement system should be within $\pm 1^\circ$, and the

resolution of the temperature measurement system should be at least 0.1° . Lab-based pH measurements are typically conducted at $25 \pm 2^\circ$ unless specified in the individual monograph or elsewhere. However, temperatures outside this range are acceptable if samples are more conveniently prepared at alternative temperatures. Non-lab-based measurements may include test samples inside process pipes, vessels, tanks, and other non-standard processing conditions. It is important to note that the definitions of pH, the pH scale, and the values assigned to the buffer solutions for calibration are designed to establish a practical, operational system for comparing laboratory results. The measured pH values may not exactly correspond to those obtained by the pH definition ($\text{pH} = -\log_{10} [\text{aH}^+]$). Still, they are closely related to the activity of the hydrogen ion in aqueous solutions. If a pH measurement system is calibrated using an aqueous buffer and then used to measure the pH of non-aqueous systems, it is essential to consider that the ionization constant of the acid or base, the dielectric constant of the medium, the liquid-junction potential (which may introduce errors of approximately one pH unit), and the hydrogen-ion response of the glass electrode can all be altered. As a result, the values obtained with solutions that are only partially aqueous should be regarded as apparent pH values.

Calibration and measurements

When it comes to calibration and measurement conditions, unless specified otherwise in the monograph, all measurements should be conducted at the same temperature used for calibration, generally in the range of 20°C to 25°C , with a tolerance of $\pm 2.5^\circ\text{C}$. Adhering to the manufacturer's instructions for temperature correction is essential.

Calibration involves determining the slope (e.g. 95-105 per cent) and the offset of the measuring system. Most commercial instruments provide a "self-test" or "start-up test" that assesses parameters such as slope and asymmetry potential, comparing the results to the manufacturer's specifications. The calibration process requires using at least two buffer solutions carefully selected so that the expected pH value of the sample falls between the pH values of the buffer solutions. The pH range should be at least two units. Additionally, when measuring the pH of an intermediate buffer solution, the reading on the scale should not deviate by more than 0.05 pH units from the expected value for that solution. When

selecting reference buffer solutions, it is advisable to choose commercially available certified reference materials that have been verified to be accurate and reliable. These solutions should be traceable to primary standards, ensuring quality and consistency. It is also essential to regularly calibrate the reference buffer solutions to maintain their accuracy and reliability in various applications.

It is important to calibrate the measurement system to ensure accurate pH measurements regularly. It is recommended that the system be calibrated daily or before each series of measurements to maintain accuracy. When immersing the electrodes in the solution to be examined, it is crucial to ensure that the conditions are consistent with those used for the reference buffer solutions. This will help in obtaining reliable readings. For suspensions, emulsions, or solutions with non-aqueous or partially non-aqueous characteristics, it is essential to note that the pH readings may only be considered as approximations of the actual value when measured on a system calibrated as described above. It is essential to use suitable electrodes for pH measurements of such mixtures to ensure accuracy.

Calibrating pH measurement systems can be complex due to their nature and operation variations. To start the calibration process, it is advisable to inspect the electrodes, particularly the reference electrode and electrolyte level, if applicable. If necessary, replenish the electrolyte supply and adhere to other precautions specified by the instrument and electrode manufacturers. Following these general principles will contribute to achieving accurate pH measurements. It is essential to calibrate or verify the pH measurement system periodically. The frequency of calibration/verification should be based on the measurement system's historical performance, the pH measurement's criticality, the pH sensor's maintenance, and the measurement operation frequency. The procedure below allows for various calibration methodologies, such as two-point, multiple-point, and multiple-segment calibrations. If the pH of the buffer is sensitive to ambient carbon dioxide, use recently boiled, purified water stored in a container designed to minimize the ingress of carbon dioxide.

To calibrate the pH measurement system, it is recommended to choose three buffer solutions from Table 3, ensuring that the expected pH of the test material falls within their range.

Two buffers are used during calibration, while the third is reserved for verification. The value of the verification buffer must fall within the range of the two calibration buffers.

Thoroughly rinse the pH sensor with water and then rinse it with the first buffer solution. Ensure the sensor is rinsed multiple times with water and buffer solution for accurate readings.

Place the pH sensor in the first buffer solution at a temperature within the range specified in Table 3.

If the measuring system does not include automatic temperature measurement and compensation, manually input the temper-

ature and pH value of the buffer solution into the instrument for temperatures not listed in Table 3.

Commence the calibration process using the first buffer as the manufacturer directs.

Remove the pH sensor from the first buffer, rinse the electrode(s) with water, and then use the second buffer solution.

Immerse the pH sensor in the second buffer at a temperature within the range specified in Table 3.

Temp. (°C)	Potassium tetraoxalate 0.05 M	Potassium m hydrogen n tartrate saturated at 25 °C	Potassiumm dihydrogen citrate 0.05 M	Potassium m hydrogen n phthalatee 0.05 M	Potassium dihydrogen phosphate 0.025 M+ Disodium hydrogen phosphate 0.025 M	Potassium dihydrogen phosphate 0.0087 M + Disodium hydrogen phosphate 0.0303 M	Disodium tetraborate 0.01 M	Sodium carbonate 0.025 M + Sodium bicarbonate 0.025 M	Calcium hydroxide saturated at 25°C.
	C ₄ H ₃ KO ₈ , 2H ₂ O	C ₄ H ₅ KO ₆	C ₆ H ₇ KO ₇	C ₈ H ₅ KO ₄	KH ₂ PO ₄ + Na ₂ HPO ₄	KH ₂ PO ₄ + Na ₂ HPO ₄	Na ₂ B ₄ O ₇ , 10H ₂ O	Na ₂ CO ₃ + NaHCO ₃	Ca(OH) ₂
15	1.67	-	3.80	4.00	6.90	7.45	9.28	10.12	12.81
20	1.68	-	3.79	4.00	6.88	7.43	9.23	10.06	12.63
25	1.68	3.56	3.78	4.01	6.87	7.41	9.18	10.01	12.45
30	1.68	3.55	3.77	4.01	6.85	7.40	9.14	9.97	12.29
35	1.69	3.55	3.76	4.02	6.84	7.39	9.10	9.93	12.13
$\Delta pH^{(1)}$	+0.001	-0.0014	-0.0022	+0.0012	-0.0028	-0.0028	-0.0082	-0.0096	-0.0034
Δt									

Table 3: pH of reference buffer solutions at various temperatures.

*(1) pH variation per degree Celsius.

If the measuring system does not include automatic temperature measurement and compensation, manually enter the buffer’s temperature and the buffer solution’s pH value at that temperature into the instrument.

To finalize the two-point calibration sequence, please follow the manufacturer’s guidelines for the subsequent buffer solution.

After completing the two-point calibration process, ensuring that the pH slope and offset fall within acceptable parameters is

crucial. Typically, these parameters consist of a 90%–105% slope and an offset of 0 ± 30 mV (0.5 pH units at 25°). The pH slope and offset can be determined through software or manual methods depending on the pH instrumentation. If manual processes are employed, it is crucial to follow the supplier’s instructions for calculating the pH sensor slope/offset. If these parameters are not within acceptable limits, the sensor should be cleaned, replenished, serviced, or replaced as necessary. Following this, the two-point calibration process should be repeated.

Remove the pH sensor from the second buffer, thoroughly rinse it with water, and immerse it in the verification buffer.

Submerge the pH sensor in the verification buffer at a temperature within the range specified in Table 2.

If the measuring system does not feature automatic temperature measurement and compensation, manually input the temperature and pH value of the buffer solution at that temperature into the instrument.

At the buffer solution temperature, the pH reading should fall within ± 0.05 pH of the value in Table 1.

Operation of an instrument

Unless specified in the monograph, all test samples should be prepared using Purified Water. All test measurements should use manual or automated Nernst temperature compensation.

To prepare the test material, adhere to the instructions provided in the monograph or specific procedural guidelines. If the sample's pH is susceptible to carbon dioxide in the surrounding environment, utilize purified water recently boiled and stored in a container that prevents carbon dioxide ingress.

Rinse the pH sensor thoroughly with water and several portions of the test material.

Submerge the pH sensor in the test material to measure its pH value and temperature. It is imperative to allow sufficient time for the temperature and pH to stabilize before conducting any measurements. In the event of suspected equipment deficiencies, diagnostic functions such as glass or reference electrode resistance measurement may be available to assist in pinpointing any issues.

If necessary, consulting the electrode supplier for appropriate diagnostic tools to ensure optimal electrode function is advised. Indicators and test papers could be appropriate if approximate pH values satisfy requirements. Further information on reagents, indicators, and solutions can be found in the designated section. Standard buffer solutions are commonly utilized for compendial tests and assays. The Solutions, Buffer Solutions subsection provides detailed discussions on buffers and the composition of standard buffer solutions. It is important to note that the pH calibration buf-

fers in Table 3 should not be replaced by the information provided in this section [3].

Applications of pH measurement

In biomedical engineering

In biomedicine, pH is commonly utilized to characterize the acidity or basicity of tissues, organs, or blood. The intracellular pH is critical in various cellular, enzymatic, and tissue processes, such as ion transport, endocytosis, and muscle contraction. Monitoring changes in intracellular pH within living cells is indispensable for studying cellular internalization pathways. Deviations from normal intracellular pH levels can impact the neural system by influencing neuronal excitability, synaptic transmission, and intercellular communication through gap junctions signal cascades. Abnormal pH values have been associated with impaired cell function, growth, and division and are observed in prevalent diseases, including malignant neoplastic disease and Alzheimer's. In wound monitoring, Schneider, et al. have established that pH serves as a recognized indicator of a wound's condition and offers insights into bacterial contamination and the stage of healing [4].

Early pH meters utilized a glass electrode with a pH-dependent electromotive force (emf). This equipment comprises a pH transducer, $p\text{CO}_2$ transducer, and thermostat, each operates independently and is housed in a trolley along with a calibrating gas system for measuring $p\text{CO}_2$. pH exhibits a linear relationship with E, as measured by an electronic millivolt meter calibrated in pH units. The dissolution of CO_2 in aqueous NaHCO_3 results in a reduction in pH, where a tenfold increase in $p\text{CO}_2$ causes a pH reduction of 1.0 unit, and the logarithm of $p\text{CO}_2$ is linearly related to pH within the range of 1.5% to 100% CO_2 . The glass electrode is surrounded by an electrolyte-filled jacket that contacts the reference electrode. CO_2 diffuses through the membrane until the partial pressures of CO_2 in the sample and the NaHCO_3 solution's fragile layer reach equilibrium, leading to a pH change corresponding to the sample's $p\text{CO}_2$ level [5].

Nikolai, et al. have introduced a pH-sensitive, water-soluble fluorescent nano micellar sensor designed for biomedical applications. This sensor features highly water-soluble fluorescent micelles, serving as a highly sensitive pH probe in water and demonstrating successful internalization into tumour cells. Moreover, it has exhibited cell specificity and significantly higher photostability than a pure organic dye label, such as BODIPY.

Furthermore, a pH sensor based on polymethylmethacrylate (PMMA) optical fibres has been developed for on-body monitoring in biological fluids. This sensor has been employed to monitor biological fluids, specifically in wound healing, with detection relying on evanescent wave absorption in a thin film deposited on the fibre core [6].

In industrial process

The measurement of pH plays a crucial role in determining a substance's chemical properties and is the primary step in controlling chemical reactions. Currently, pH measurement finds application in various sectors, encompassing the chemical industry and public organizations, agricultural and fishery-related industries, and other sectors associated with water handling. Industries rely on pH measurements to ensure product quality.

The effectiveness of high-pressure treatments in food processing is often linked to pressure-induced pH changes. The pH of selected liquid foods at 25°C was monitored in situ under high hydrostatic pressure up to 800 MPa using a previously validated high-pressure pH sensor. The results showed increased acidity in all tested food and water samples as the pressure was elevated [7].

In the electricity and electrochemistry industry, pH measurement is utilized in processes such as plating, etching of metal surfaces, and assembly of batteries. The control of pH in a plating solution significantly impacts the final finish. Without proper pH control, the plated finish may be prone to peeling and may not achieve the desired colour and sheen. The anodic oxidation process is employed in coating cooking utensils to create a film-like coating similar to that on aluminium objects; maintaining precise pH levels in the processing solution is essential to achieve the desired finish. This holds particularly true for industries such as paper and pulp manufacturing, where pH measurement is conducted more frequently and continuously than in any other industry. The wastewater at pulp and paper plants contains effluents from various operations, including pulping, bleaching, paper making, and recycling. To treat this wastewater, it undergoes a process where suspended solids are separated and precipitated in a precipitation tank using flocculation agents. Proper pH levels are crucial during this procedure to minimize chemical consumption and prevent equipment corrosion [5].

Maintaining the proper pH is critical for product testing in the textiles and dyeing industry. The dye bath's pH significantly influences the dye's permanence and processing speed. We are incorporating a pH indicator into a nylon nanofibrous structure by adding dye to the polymer solution before the electro-spinning operation can be instrumental. This advancement could potentially lead to the development a textile pH sensor with extensive applications [8].

Conclusion

When conducting pH operations, it is essential to prioritize accuracy and precision. This can be achieved by thoroughly defining analysis requirements, ensuring strict compliance, and minimizing the impact of pH on overall analysis uncertainty. By employing meticulous calibration, assessing repeatability, and evaluating accuracy, we can confidently ascertain the smallest quantity of solution required for optimal results.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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