

pH Measurement of Pure Water Performance of Specialist Sensors



The pH measurement of purified water samples needs special attention as mentioned in the ASTM D5464 standard. METTER TOLEDO offers two specialist sensors InLab® Pure Pro-ISM and InLab® Pure for the pH measurement of such low ionic samples. The technical suitability of these sensors is verified by evaluating accuracy, precision, and response time in pure water samples. Compared to standard pH electrodes they show a remarkable better performance.

1. Introduction

Purity of water is an important aspect in majority of industrial sectors^{1,2}. Industries like pharmaceutical, semiconductor and electronics, power plants, and life sciences require pure water for their day-to-day laboratory testing and process activities. pH of water becomes a critical parameter in many applications at different workplaces in these industries, since it indicates the amount of soluble trace minerals, ability to corrode metals, suitability for aquatic life, and quality of potable drinking water. Hence, to address this concern, ASTM D1293 describes the method to measure pH of water². At 25 °C, pure water is expected to measure a neutral pH value of 7.0, but this majorly varies due to absorption of CO₂ from atmosphere and lack of sensitivity of pH sensor to record the correct pH reading. Water normally shows a pH of 5.5 to pH 8³. On equilibrium with air, pH of pure water can drop to 5.2 due to the formation of carbonic acid.

The measurement of pH in pure water samples is critical due to its low conductivity, fluctuations in liquid junction potential of electrode, and also lack of sensitivity of glass membrane. Pure water can be defined as water samples with a conductivity of less than 100 µS/cm. These pure water samples are low in both hydrogen ions and conducting ions. Low ionic concentration of the sample deters a stable liquid junction potential in the pH electrode system. The ASTM D5464 method focuses on pH measurements in low ionic water samples with a conductivity of 2 to 100 µS/cm⁴. Using specialist laboratory pH sensors from METTLER TOLEDO eases pH measurement in such low ionic water samples. The following study is a technical approach to measure pH in low ionic water samples using pH sensors of various types including specialist sensors.

2. Experimental

A. Chemicals and reagents

The following water samples were used: tap water, packaged drinking water, low ionic conductivity standard (84 µS/cm), distilled water, and de-ionized water from Milli-Q® Direct system (ultrapure water Type 1). METTLER TOLEDO buffers of pH 4.01 and 7.00 were used for the calibration of the sensors. The conductivity standard 84 µS/cm was used for the calibration and verification of conductivity sensor.

B. pH and conductivity measurement apparatus and instrumentation

A SevenExcellence S470 meter (version 4.1.4) was used for all the pH and conductivity measurements. The pH of the water samples was measured using three generalist pH sensors named InLab Routine Pro-ISM, InLab Expert Pro-ISM, and InLab Max Pro-ISM and the two specialist sensors InLab Pure and InLab Pure Pro-ISM designed for pH measurement of pure water. "Pro" stands for inbuilt temperature probe; "ISM" (Intelligent Sensor Management) feature ensures storage and transfer of calibration history and sensor information. The conductivity of the samples was measured using the conductivity sensor InLab 741-ISM. For samples having conductivities below 100 µS/cm, the pH and conductivity measurements of these samples were carried out in a glass flow-cell to limit the samples exposure to atmospheric gases. The data collection and analysis were processed using LabX 2018 PC software (version 9.0.0).

C. Procedure

All the pH sensors were calibrated using the two pH buffers. The conductivity sensor calibration was performed using the conductivity standard 84 $\mu\text{S}/\text{cm}$. Firstly the conductivity of the samples was determined. The pH measurement of all samples was repeated three times. Some interval pH measurements were carried out to study the variance of pH over time with an interval of 15 seconds. The experiments were carried out in a laboratory with an ambient temperature of 25 ± 2 °C.

3. Result and Discussion

Experimentally acquired pH data by various pH sensors for all samples is plotted in the graph (figure 1). A correlation is drawn with respect to their conductivity. Each sample behavior is discussed individually to focus on the factors affecting accuracy and precision of pH measurement in these samples. The advantages offered by METTLER TOLEDO specialist sensor in measuring pH of these samples are further elaborated.

a) Tap water

The pH for this sample was observed to be within 7.6 – 7.9 pH units. This pH value may differ from place to place and the variation in pH may depend on municipalities and their pipeline systems. An average conductivity of 121 ± 5.4 $\mu\text{S}/\text{cm}$ was recorded for the sample. Tap water normally contains dissolved inorganic salts. The major ions that contribute to elevation in pH and conductivity of these samples are the cations calcium, magnesium, sodium, and potassium and anions chloride, sulphate, carbonate, and bicarbonate^{5,6}. The average response time of all used sensors to measure the pH was about 4 minutes whereas the InLab Pure Pro-ISM sensor could measure it within 30 seconds.

b) Packaged drinking water

The measured pH values of this sample were observed to be significantly stable among all the five pH sensors. An average pH value of 6.65 ± 0.02 was noted excluding one pH sensor which measured an elevated pH reading of 6.8 pH units. The conductivity of the sample was 75.6 ± 2.2 $\mu\text{S}/\text{cm}$. The average response time was less than 90 seconds. The stability in pH and conductivity measurement of this water sample is attributed to the fortification of this packaged water with natural minerals and controlled monitoring of pH and conductivity during the bottling process⁷.

c) Low ionic conductivity standard (84 $\mu\text{S/cm}$)

This sample has a known conductivity value of 84 $\mu\text{S/cm}$ and hence known amount of KCl (0.56 mmol/L). However due to its low ionic content that does not significantly contribute to the pH value, the sample behavior was observed to be similar to pure water samples. A low pH in the range of 5.2 to 5.6 was observed, owing to the exposure with atmospheric CO_2 . An average response time of more than 2 minutes was recorded for all sensors.

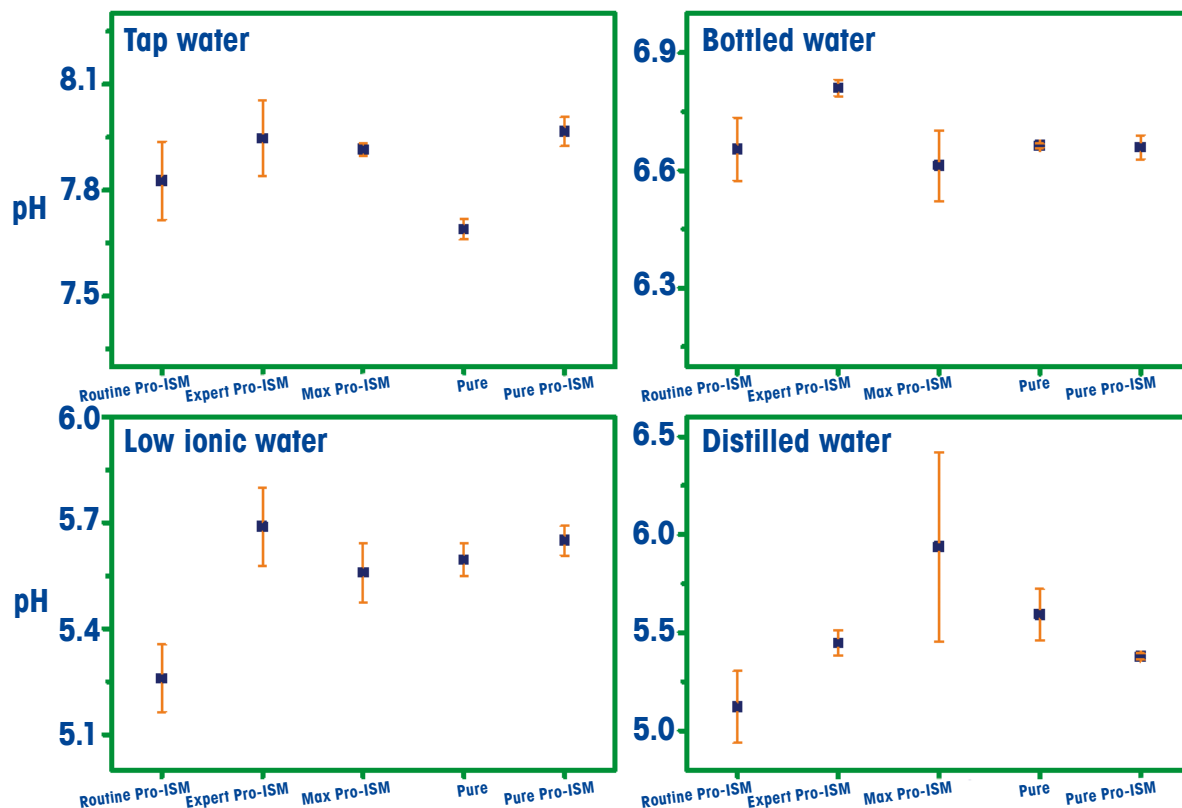


Figure 1: Graph showing pH value for each InLab sensor in different water samples. The error bars denote the standard deviations in the pH measurement.

d) Distilled water

With an average conductivity of 2 $\mu\text{S/cm}$, this water sample is vulnerable to atmospheric CO_2 and rapidly absorbs CO_2 gas. The pH value was found to be in the range of 5.1 to 5.9. An average response time of 94 seconds was observed. Hence the pH of the sample recorded was low compared to the theoretically expected value of pH 7. A different measurement setup that can avoid this seep-in of CO_2 from the atmosphere would be required for this sample.

e) De-ionized water

The de-ionized water sample is an example of pure water with the least conductivity. The pH measurement of this sample showed a similar pattern as seen for distilled water sample. The pH change was drastic ranging from expected pH of 7.0 to experimentally obtained value of 5.8 ± 0.3 pH units and the corresponding conductivity values were 0.3 ± 0.25 $\mu\text{S/cm}$. This pH value is in agreement with the expected pH value when exposed to atmospheric CO_2 of up to 300 ppm⁸. Maximum response time to measure this sample was 4.5 minutes.

Additional setup for measuring pH of pure water samples

For pure water samples, one of the major reasons of a pH value below 7.0 is atmospheric carbon dioxide interaction with the sample. Hence pH of a given sample can differ erratically at a given time. To minimize the exposure of high purity water to atmosphere, use of flow-cell is recommended. Following graph illustrates the pH of deionized water measured using a flow cell against an open beaker pH measurement. The water source was directly connected to the flow-cell for the pH determination.

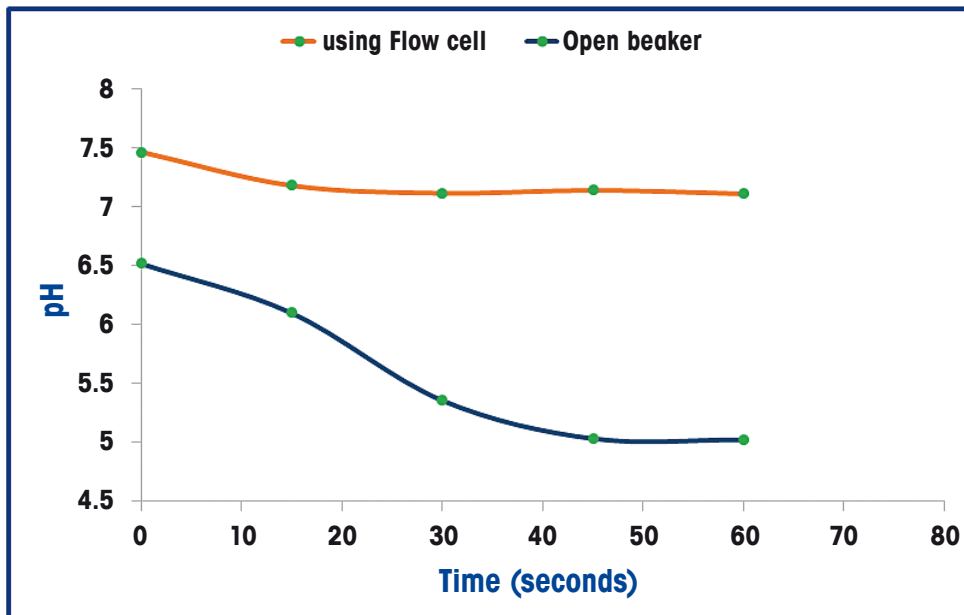


Figure 2: pH value recorded for fresh de-ionized water using a flow-cell, in comparison with pH measured in an open beaker.

For distilled water, since the sample was already stored in a container, to ensure a closed setup with no atmospheric CO₂, the sample is initially collected in glass flask and heated up to 75 °C to degas it. N₂ gas was purged into the sample while the sample was cooled down to 25 °C and the pH of the sample was measured. For easy controlling of temperature and purging of inert gas, the METTLER TOLEDO EasyMax reactor setup was used in this study. It is a 100 mL capacity multi-neck, glass cylinder reactor jacketed in a thermostat with clamped cover having opening for the pH electrode and provision for temperature regulation, stirring, and gas purging.

The pH values recorded for distilled and de-ionized water using suitable additional setup as discussed above, in combination with the specialist sensors are mentioned in table 1. The experimental values obtained by these setup, matched the expected theoretical pH values and the maximum response time taken by the specialist sensors were 70 seconds.

Sample	InLab Pure Pro-ISM			InLab Pure		
	Mean pH	Standard deviation	Average response time	Mean pH	Standard deviation	Average response time
De-ionized water	7.45	0.05	42 sec	7.24	0.09	70 sec
Distilled water	6.99	0.02	11 sec	6.96	0.01	25 sec

Table 1: pH measurements of the pure water samples (n = 3).

Features of specialist sensors

METTLER TOLEDO offers two specialist sensors InLab Pure and InLab Pure Pro-ISM for low ionic and pure water pH measurement in laboratory. They have been designed to achieve ideal sensitivity for delivering accurate and precise pH measurements of such samples. The sensors have an immovable glass sleeve junction for the reference electrolyte which ensures a steady out-flow of electrolyte into the pure water samples. They have a LoT glass membrane for pH sensing that is very sensitive due to its low resistance of less than 50 MΩ at 25 °C. The glass membrane shape is spherical to render more sample interaction and thus further boosting its sensitivity. InLab Pure Pro-ISM has an added benefit of a bridge electrolyte wherein the inner reference electrolyte is 3 mol/L KCl and the outer bridge electrolyte is 1 mol/L KCl. The electrolyte flow with lower concentration of KCl stabilizes the junction potential faster compared to the conventional reference electrolyte concentration. This improves the response time in measuring pH of such low conductivity water samples. In case of InLab Pure sensor, the reference electrolyte is FRYSCOLYT-B (2:1 mixture of glycerin and 3 mol/L KCl). This reference electrolyte facilitates pH measurement by negating the sudden jump of junction potential formed while using a conventional 3 mol/L KCl reference electrolyte.

Normally the pH electrodes designed for general lab applications are not sensitive enough to measure pH of low ionic and pure water samples. For an accurate and precise pH measurement of pure water samples, factors like type of pH glass membrane, shape of glass tip, and type of junction play important roles. Precision of the specialist sensors in measuring the pH of these water samples are evident from table 2. A standard deviation of less than 0.05 pH units indicated consistent precision in pH measurement with these specialist sensors. For generalist sensors, the precision varied in a range of 0.02 to 0.48. For pH measurement of pure water, an additional setup like a flow-cell and inert gas purging are recommended to achieve accurate results.

Sample	Routine Pro-ISM	Expert Pro-ISM	Max Pro-ISM	Pure	Pure Pro-ISM
Tap water	0.11	0.11	0.02	0.03	0.04
Bottled water	0.08	0.02	0.09	0.01	0.03
Low ionic water	0.09	0.11	0.08	0.04	0.04
Distilled water	0.18	0.06	0.48	0.03	0.02

Table No. 2: Standard deviations in pH measurements of different sensors. Precisions within ± 0.05 pH units are marked in green.

4. Tips and Hints

- Make sure all the containers and tubings used during the pH measurement are clean and well rinsed with deionized water to avoid any contamination.
- For the pH measurement of pure water, take maximum care to avoid any exposure to air and atmospheric CO₂ even during sample handling. If possible, measure the sample directly from the source and use glass containers. Limit the sample storing time to a minimum.
- Caution should be maintained while measuring the pure water samples to limit the exposure of sample to electrolyte solution outflowing from the electrode, as it can disturb the original ionic concentration of the sample and hence affect the pH value. However, the continuous flow of water in the flow-cell limits the exposure time and hence minimizes this effect on the measurement results.
- Between the measurements or when the electrode is not in use, the electrode should be kept in wetting cap filled with InLab storage solution. This helps in reconditioning of glass membrane by enriching it with ions. Never leave it or store it in pure water.
- Make sure that the electrolyte filling hole is open during pH calibration and measurement. This applies for the inner and outer electrolyte filling hole for InLab Pure Pro-ISM.
- Ensure the use of fresh buffers for electrode calibration.
- Regular maintenance is very important for prolonging the lifetime of pH electrode. The electrolyte needs to be refilled regularly.

5. Conclusion

pH measurements of pure water samples possess various challenges. The fewer the concentration of dissolved ions in the water sample, the higher is the probability of obtaining an incorrect pH result. Uptake of CO₂ from air and carry-over of ions from different samples or glass ware affect the pH value of pure water more than general samples. Most of them can be minimized by careful working and protecting the sample from air.

The variance in pH results also depends on the sensor design. Hence choosing the right sensor is of utmost importance and directly influences the overall quality of pH measurement. InLab Pure and InLab Pure Pro-ISM are ideal for measurement in water samples, giving precise pH results and hence can be termed as 'water specialist sensors'. These sensors offer highest precision and fast response time, provided the pH of the sample is stable or being measured in a controlled setup.

6. References

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