

pH in Seafood Processing

InLab Solids Pro-ISM Sensor

pH measurement of seafood correlates with its freshness and is useful to estimate its shelf life for the canning and seafood processing industries. Currently, measuring the pH is cumbersome and time consuming due to the sample preparation involved. A conventional pH sensor with a ceramic junction gets easily clogged and is difficult to clean, leading to sensor fouling and inaccurate results. By adjusting the sensor design, like in METTLER TOLEDO's InLab Solids Pro-ISM, the functional components of the sensor are modified to allow measurement of seafood samples by direct insertion. The features like open junction, solid electrolyte, spear shaped sensor tip and a sensitive pH membrane give an overall faster and reliable approach to pH determination in these samples.



Introduction

Seafood owes its authentic taste and flavor to its freshness. The time passed after catch and the temperature it had been stored at serve as key factors in determining the final quality and typical characteristics of seafood products. The changes in biochemical components of fish leads to a change in its pH value. Hence, the quality deterioration and shelf life prediction for the seafood can be adequately estimated using pH and temperature recorded for that sample.



Figure 1: Seafood on display

Importance of pH Measurement

The pH measurement of seafood products help to assign the proper storage conditions. The average pH value for fresh seafood is 6.2, though it may vary according to the type of fish. Scientific studies found direct correlation between the pH and freshness of seafood. The study found the pH of frozen seafood rising after it crossed the expiry date mentioned on the product's package, indicating the onset of spoilage. The pH value reached 6.6 within seven days due to the production of alkaline bacterial metabolites. Increase in these metabolites can be confirmed by estimating the total volatile nitrogenous bases in seafood samples. This assay is used as a routine chemical analysis to evaluate the degree of spoilage in seafood samples. The canning industry needs the pH information of the fresh seafood for efficient canning. pH value is recorded throughout to maintain batch consistency.

Measurement Challenges

Seafood's solid sample nature requires sample preparation before proceeding for pH measurement when a classic sensor is used. This preparation is tedious

and involves mincing the seafood meat and blending it into a paste. Such sample preparation procedures leave a high probability of errors. Moreover, the physical cutting and grinding can lead to altered pH value. Unstable pH values due to sensor fouling is another common problem faced for such samples.

The table below outlines the challenges and negative effects on pH measurement results when using a typical sensor for seafood samples.

Sample Challenge	Sample Impact
Solid sample nature	Direct insertion into the sample is difficult
Sample preparation	Alternate method includes grinding and blending of seafood sample and is time consuming.
High protein sample content	Sensor junction damage due to clogging, causes inaccurate results.
High fat sample content	Sensor fouling due to deposition on the glass membrane, causes sluggish response.

High fat and protein content of seafood can accumulate on the sensor membrane, thereby preventing the sample from interacting with the membrane to initiate a signal. Further, when proteins from the sample interact with conventional liquid reference electrolyte, the proteins precipitate due to free silver ions from silver/silver chloride reference system. When such precipitation occurs, a typical ceramic fritted junction will clog, preventing electrolyte from further mixing with the sample and thereby causing measurement error.



Figure 2: Sample impact on a conventional pH sensor having a ceramic junction

The solid nature of seafood can introduce sample-handling challenges for the user. Most of the time, pH

has to be measured for cold stored seafood samples. Delicate sensing membranes can be broken during the measurement process. For this reason, alternate methods of indirect measurement techniques, wherein the sample is grinded with water prior to measurement and is blended into paste. However, the dilution process affects the pH measurement results, yielding inaccuracies. The most accurate method of pH measurement is direct measurement, where the sample remains unaltered and the pH sensor is in equilibrium with sufficient amount of sample.

Reliable pH with Easy Piercing

InLab Solids Pro-ISM (51344155) is a specialist sensor for measuring pH of seafood in terms of accuracy and precision. The pH sensing membrane is constructed from low temperature (LoT) glass, which yields fast results and is resistant to breakage. The solid XEROLYT®EXTRA polymer reference system offers two benefits: it is low maintenance, and has a clog-free open junction, which eliminates the risk of protein fouling.



Figure 3: InLab Solids Pro-ISM pH sensor

The spear-shaped sensor tip design enables easy piercing into the solid samples. The sensor features an improved reference system, ARGENTHAL™. The silver ion trap in it takes care of silver ions from migrating into the electrolyte. The proteins from seafood sample can now freely interact with the electrolyte without precipitation.

The sensor has Intelligent Sensor Management (ISM) technology that offers data security, stores calibration history and monitors maximum temperature exposure of the sensor. 'Pro' stands for a built-in temperature

probe in the sensor that helps to capture the sample temperature accurately and supports the ATC (automatic temperature compensation) functionality. pH measurements are highly temperature dependent. For an accurate pH value, the pH calibration slope needs to be corrected to measurement temperature. By the virtue of ATC, this is attained so as to take care of the influence of temperature dependence on the sensor and pH system. For example, while measuring a sample at 15 °C, the right temperature ensures the calibration slope is corrected to represent the system performance at 15 °C. However, the pH value measured at 15 °C would differ from the pH value at 35 °C, as the ionic activity of the sample varies with temperature.

Procedure and Method

Calibrate the sensor using MT buffers that bracket the sample range (in this case pH 4.01 and 7.00). Record the calibration slope and offset value for the electrode. A slope value of 95 -105% and an offset of 0 ± 30 mV ensures reliable measurement.

A small representative of seafood sample is taken for analysis. Measurements through direct insertion into the seafood meat without slicing of a piece is also possible. In both cases, the seafood sample must be punctured with InLab Solids Pro-ISM such that the reference junction at the shaft has proper contact with the seafood mass. Repeat the measurement at various positions to obtain a representative pH reading. A standard deviation within ± 0.05 pH units indicates fair variance in the pH measurement. Repetitive measurements increases the chances of protein build-up and can lead to contamination of the sensor surface. Hence, proper care and maintenance of the electrode is necessary and helps to overcome the sluggish behavior, if any.



Figure 4: Measurement of seafood sample using InLab Solids Pro-ISM pH sensor.

Results

The pH value of different seafood samples were recorded at ambient temperature using InLab Solids Pro-ISM sensor. Average pH values for all the samples (in triplicates) are given in below table.

Sample	Mean pH value	Std. Dev.	Avg. time (s)
Kingfish	6.24	0.03	38
Sardines (canned)	6.53	0.01	06
Tuna chunks (canned)	5.92	0.01	06

Expert Tips

- Clean the electrode regularly to remove accumulated fat and protein. For thorough cleaning, wash the electrode with mild soapy solution, and later rinse it with de-ionized water.
- Regular maintenance is very important for prolonging the lifetime of pH electrode. Periodic reconditioning of the electrode in 0.01M HCl is recommended, based on the sensor performance. Frequency of reconditioning would depend upon the number of samples analyzed per day and life of the sensor. Old sensor requires more frequent conditioning compared to a newer sensor. Remember to re-calibrate the sensor after reconditioning.
- It is recommended to soak the sensor in pepsin/HCl solution (51350100) for one hour once a week to remove protein build up on the glass membrane.
- The pH range for this sensor is 1 to 11 pH units and hence should not be exposed to harsh acidic or alkaline chemicals.
- In between measurements or when the electrode is not being used for brief period, it is best to keep the electrode in wetting cap filled with InLab Storage Solution (30111142).
- Never store the electrode dry or in distilled water, as this will affect the pH-sensitive glass membrane and thus shorten the lifetime of the electrode.
- Ensure use of correct buffers in the correct sequence. Always use fresh buffers. Check expiry date.

Further Information

- Electrode handling movies on:



- Comprehensive range of pH meters, electrodes, solutions, and accessories:

► www.mt.com/pH

References

- Abbas, K.A., Mohamed, A., Jamilah, B. and Ebrahiman, M., 2008. A review on correlations between fish freshness and pH during cold storage. American journal of biochemistry and biotechnology, 4(4), pp.416-421.
- M. Kayim and E. Can, 2010. The pH and Total Fat Values of Fish Meat in Different Iced Storage Period. Asian Journal of Animal and Veterinary Advances, 5: 346-348.

Mettler-Toledo GmbH, Analytical

Im Langacher 44
8606 Greifensee, Switzerland
Tel. +41 22 567 53 22 / Fax +41 22 567 53 23

Subject to technical changes
© 05/2019 METTLER TOLEDO. All rights reserved
Document Number 30553182
Group MarCom 2724 AG

www.mt.com/pH

For more information