Measuring pH of concentrated samples

Keywords
pH, concentrated samples, seawater, brines, food, acids, bases, high ionic strength.

Goal
The following application note describes the challenges, best practices and recommended instrumentation when measuring pH in high ionic strength, or “concentrated” samples.

Introduction

In pH measurement, we sometimes measure samples with low ionic strength (such as pure water or betaine solution), or high ionic strength (such as seawater, food, or other concentrated samples). These sample types can be challenging, but when you understand best practices, you will be successful in your measurements.

Ionic strength

Ionic strength is a function of the concentration and charge of all the ions in a solution. The precision and bias of pH measurements in samples with low or high ionic strength may be affected, unless proper procedures are observed.

Ionic strength is an important factor in many processes. It is essential in the function of all living organism, in environmental and biochemical reactions, etc. As noted, ionic strength plays an important role in a pH measurement.

Low ionic strength samples, such as pure and surface waters, sugar or betaine solutions, present their own unique challenges in pH measurement (See Application Note AN006 on “Measuring pH in Low Ionic Strength Solutions”).

High ionic strength samples, such as seawater, brines, strong acids, strong bases, foods, and beverages also present challenges, such as:

1. Change in hydrogen ion activity — ion mobility decreases in the high ionic strength samples and the activity differs from the concentration. (Note: the pH electrode responds to hydrogen ion activity, not the concentration).
2. High ionic strength solutions change the liquid junction potential of the pH electrode. This may lead to bias and considerable time may be required to establish a stable reading.

Determine the ionic strength of your sample

Theoretically, the ionic strength of a sample can be calculated by multiplying the concentration of each ion by the corresponding squared charge on the ion, then summing and dividing by two. But that's not much fun nor easy to do.

From a practical point of view, there are other indicators, such as conductivity and concentration that can provide a rough estimate of a sample's ionic strength. There are no exact conductivity and concentration value rules for low and high ionic strength, but we can make general categories (high, routine and low) and choose the best approach for pH analysis of extreme ionic strength samples (high or low).

Common Ionic strength examples

High ionic strength examples
• Sea Water; 0.8M (53 mS/cm)
• 0.5M KCl (59 mS/cm)
• 1% NaOH; 0.25M (53 mS/cm)
• 10% brine NaCl (140 mS/cm)
• 20% nitric acid (763 mS/cm)
• 20% H_3PO_4 (123 mS/cm)
Routine ionic strength examples
• Industrial Wastewater (5 mS/cm)
• 0.05M pH 7 buffer (6.2 mS/cm)
• 0.05M pH 4 buffer (4.4 mS/cm)
• 0.05M pH 10 buffer (6.3 mS/cm)
• 0.05M KCl (6.7 mS/cm)
• 5400 ppm Total Dissolved Solids (10 mS/cm)
Low ionic strength examples
• Pure water in air (1 µS/cm)
• Rain water (50 µS/cm)
• Tap water (500 µS/cm)
• 0.05mM H_2SO_4 (38 µS/cm)
• 0.67mM KCl (100 µS/cm)
• 50 ppm Total Dissolved Solids (~100 µS/cm)

Tips for testing concentrated samples with high ionic strength

The pH measurement challenges in low or high ionic strength samples can be overcome by using the appropriate testing procedures.

The following techniques can be recommended for optimizing pH measurement in high ionic strength samples:

- Use a fast-flowing, low resistance junction, such as sleeve junction or capillary junction.
- Use a strong salt filling solution (**Note:** the 3M or 4M KCl fillings solutions that are used in Orion pH electrodes are close to saturation, so this is about as strong as you can go).
- If additional improvements are desired, use a double-junction electrode, like an Orion ROSS model, which can protect the reference from salt intrusion and allow modification of the fill solution to better match the sample, although modification is not usually necessary.
- For example, for samples with a pH less than 2 or greater than 12, adding a slight amount of the acid or base to the filling solution to adjust the pH and make it more compatible with the sample should decrease electrode stabilization time.
- For samples with a high salt content, it is possible to use a strong filling solution using the same salt as the sample.
- Consider equilibrating the electrode in a high-ionic strength solution before using to test concentrated samples. The equilibrating solution can be one or more portions of the test sample itself or a prepared solution of similar composition to the test sample(s).
- Stir the samples and allow sufficient time for the electrode to respond, since salty samples tend to drift as equilibrium is established at the junction. Using a timed reading, for example, 5.0 minutes after starting the measurement, can make results more repeatable.
- Use a high salt buffer for calibration or to check accuracy (for example, TRIS buffer in synthetic seawater).
- For the best results, keep the calibration standards and sample temperatures within 2°C of each other.
- Use an automatic temperature compensation (ATC) probe or a triode pH electrode with built-in ATC to monitor temperature.

We recommend using the following pH Electrodes:

- Thermo Scientific™ Orion™ ROSS™ Sure-Flow™ pH Electrode 8172BNWP
- Thermo Scientific Orion ROSS Ultra™ Low Maintenance pH/ATC Triode™ Combination Electrode 8107BNUMD
- Thermo Scientific Orion Sure-Flow pH Electrode 9172BNWP

Thermo Scientific Orion Star A2114 Meter Kit (Cat. No. STARA2114) including calibration standards and ROSS Sure-Flow pH Electrode.

Conclusion

Although measuring pH in concentrated samples can be challenging, understanding and employing best practices can ensure that you can be confident in the accuracy of your measurements.

Ordering information

Product	Description	Cat. No.
Meter	Thermo Scientific Orion Versa Star Multi-parameter Benchtop Meter	VSTAR93
	Thermo Scientific Orion Versa Star pH Benchtop Meter	VSTAR12
	Thermo Scientific Orion Star A211 pH Benchtop Meter Kit	STARA2114
Electrode	Thermo Scientific Orion ROSS Sure-Flow pH Electrode	8172BNWP
	Thermo Scientific Orion ROSS Ultra Low Maintenance pH/ATC Triode Combination Electrode	8107BNUMD
	Thermo Scientific Orion Sure-Flow pH Electrode	9172BNWP
Solutions	Thermo Scientific Orion ROSS pH Electrode Filling Solution	810007
	Thermo Scientific Orion Silver Chloride Electrode Fill Solution	900011
	Thermo Scientific Orion pH Electrode Cleaning Solution D	810007
	Thermo Scientific Orion General Purpose pH Electrode Cleaning Solution C	900023

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