

Measuring pH of Concentrated Samples

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Key Words

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 know the 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 006 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. We are faced here with two challenges:

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. 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 and not easy to do.

From a practical point of view, there are other indicators that can provide a rough estimate of a sample's ionic strength. These other indicators include conductivity and concentration. 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).

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 $\mu\text{S}/\text{cm}$)
- Rain water (50 $\mu\text{S}/\text{cm}$)
- Tap water (500 $\mu\text{S}/\text{cm}$)
- 0.05mM H_2SO_4 (38 $\mu\text{S}/\text{cm}$)
- 0.67mM KCl (100 $\mu\text{S}/\text{cm}$)
- 50 ppm Total Dissolved Solids (~100 $\mu\text{S}/\text{cm}$)



The chart to the left shows common examples of samples with various levels of ionic strength. Examples range from high to mid-range to low ionic strength values.



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 which can protect the reference from salt intrusion and allow modification of the fill solution to better match the sample.
- The Orion pH electrode filling solution (Cat. No. 810007) of the ROSS 8172BNWP or 800300 reference half cell may be modified to match the sample composition.

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, use a strong filling solution using the same salt as the sample.

For example, when measuring the pH of sodium bromide brines, use sodium bromide as the filling solution.

- Allow sufficient time for the electrode to respond, since salty samples tend to drift as equilibrium is established at the junction.
- Use a high salt buffer (for example, TRIS buffer in synthetic seawater). For preparation instructions, please read “Determination of the pH of sea water using a glass/reference electrode cell” prepared by the US Department of Energy’s Carbon Dioxide Information Analysis Center (CDIAC) - <http://cdiac.ornl.gov/ftp/cdiac74/sop06.pdf>
- 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™ ROSS™ Half-Cell Electrode 8101BNWP and 800300 Sure-Flow reference half cell
- Thermo Scientific Orion Sure-Flow pH Electrode 9172BNWP



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.

To purchase Thermo Scientific Orion pH meters, electrodes and other related products, please contact your local equipment distributor and reference the part numbers listed below.

Product	Description	Part Number
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	STARA2115
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
	Thermo Scientific Orion ROSS pH Half-Cell Electrode and Thermo Scientific Orion ROSS Sure-Flow Reference Half-Cell Electrode	8101BNWP and 800300
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

Visit www.thermoscientific.com/water for additional information on Thermo Scientific Orion products, including laboratory and field meters, sensors and solutions for pH, ion concentration (ISE), conductivity and dissolved oxygen analysis plus spectrophotometry, colorimetry and turbidity products.

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