Application Note 007

Measuring pH of Non-Aqueous and Mixed Samples

Water Analysis Instruments, Thermo Fisher Scientific

Key Words
Non-aqueous samples, mixed aqueous samples, pH measurement, organic solvents, paints, coatings, petroleum products, edible oils, ethanol, food and beverage testing.

Goal
The following application note describes the challenges and best practices when measuring pH in non-aqueous and mixed samples.

Introduction
Although pH measurements are primarily done on aqueous (water-based) samples, there are many pH applications that call for pH measurements and titrations in non-aqueous samples or in mixed aqueous/non-aqueous samples.

These sample types can be challenging, but when you know the best practices, you will be successful in your measurements.

Challenges of Non-Aqueous pH Testing
Can you use the same pH electrode and the same testing procedure for non-aqueous samples as for aqueous samples? Not necessarily. There are some challenges to be met when testing non-aqueous or aqueous/non-aqueous mix samples, such as unstable readings and drift, long response times, and measurement errors.

Examples of Non-Aqueous Sample Testing
Below is a list of common non-aqueous and mixed aqueous/non-aqueous samples that are frequently tested:

- Paints and coatings, inks
- Petroleum products, oils, isoparaffinic solvents
- Amines in petroleum products, TAN and TBN titrations (ASTM D664[1] and ASTM D2896[2])
- Edible oils, butters, low water content lotions
- Engine coolant, anti-rust, ethylene glycol, monoethylene glycol
- Pharmaceuticals - weak base titrations with perchloric acid in glacial acetic acid
- Bioethanol and biodiesel, alcohol, acetone
- pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol (ASTM D6423[3])

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Factors that contribute to measurement errors when measuring non-aqueous samples:

1. The glass bulb of a pH electrode depends on a hydrated gel outer layer to sense the hydrogen activity (and pH) of a solution. When this hydrated layer is dehydrated or disrupted, response can become slow and precision may be lost.
2. The aqueous fill solution of the pH electrode may not be miscible or may not dissolve into the sample being tested. If that happens a junction potential may develop and introduce bias to the results.
3. The sample may be incompatible with the pH electrode construction. The body of the pH electrode may be degraded by the sample being tested. The gelled solution in a non-refillable electrode may be subject to degradation by some non-aqueous samples.
4. The sample may have high impedance and be a poor electrical conductor. This challenges the measuring system electrical components. The measuring system must have a sensitive, high impedance pH meter, a relatively low-resistance glass pH sensing bulb, and a well-constructed pH electrode with good insulation resistance to ensure that the correct signals are measured.
5. The aqueous buffers commonly used for pH calibration are not directly translated to a non-aqueous pH scale. In some cases, non-aqueous buffer recipes are available. But for many non-aqueous samples, pH will be a relative value that may not correlate directly to the aqueous pH value. Note that in the case of a titration, this issue does not apply, unless the endpoint is based on an absolute pH value.

Best Practices for pH testing in Non-Aqueous or Mixed Samples

By making good equipment choices and observing best practices, you will obtain the best possible results for your pH testing and pH titrations in non-aqueous and mixed samples. Here are our recommendations:

Equipment

Choose a good quality pH meter and electrode.

- Pen-type, pocket pH testers and disposable pH electrodes with non-refillable references are not good choices for these challenging samples due to design and construction.
- Choose a glass-body pH electrode with a refillable double junction construction and adequate flow that makes good contact with the sample, is easy to clean, responds quickly, and has a relatively low-resistance glass pH sensing bulb.

When measuring non-aqueous samples, we recommend the Thermo Scientific™ Orion™ ROSS™ Sure-Flow™ pH Electrode 8172BNWP with a Thermo Scientific™ Orion™ Versa Star™ Multi-parameter Benchtop Meter.

The Orion 8172BNWP is a specified by ASTM D6423 Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol.

Sample Treatments

In some cases, it may be advisable to alter the sample to provide for a better pH measurement.

For example, ASTM D4980 for pH in Waste[4] recommends that non-aqueous liquids be prepared as follows: make a 10% mix of waste in water and measure the pH of the aqueous portion.

Another source suggests adding a small amount of neutral electrolyte (such as a quaternary ammonium salt) to the sample may be advantageous for high resistance samples.[5]

pH Electrode Preparation and Maintenance

Filling Solution

Use an alternate filling solution in the refillable double junction pH electrode to improve the speed and precision of the measurement for many non-aqueous samples, especially titrations. Note that water-miscible samples such as alcohols and alcohol-water mix samples may not require an alternate filling solution.

Use the alternate fill solution specified by your test protocol, or a "universal" fill solution of 1-3M lithium chloride in ethanol or ethylene glycol, which is good for most applications.

Keep the level of the fill solution at least one inch (25 mm) above the level of the test solution to ensure good positive flow from the junction into the sample.

Storage

Store the electrode in the aqueous storage solution recommended by the manufacturer. This ensures proper rehydration and conditioning of the bulb. Do not leave the electrode in the non-aqueous sample for any extended period of time, as this can degrade the hydrated gel layer of the pH bulb.

Between samples, store briefly in DI water, or store in storage solution for longer periods.

In some cases, place the electrode into pH buffer between samples and wait for the correct pH reading before proceeding.

Cleaning and Maintenance

Perform maintenance and cleaning appropriate for the sample. This can be done on a schedule or when performance is impacted (too slow, drifty, noisy, or not reproducible).

If the samples are oily, use a buffered detergent cleaner (Cat. No. 900024). For general cleaning and regeneration, use a general purpose pH electrode cleaning solution (Cat. No. 900023).

Drain and refill the electrode weekly or more frequently. Keep fill level more than 25 mm above sample for positive flow into the sample and to protect from intrusion.

Recommended Testing Techniques

Use proper rinsing technique. After each sample test, rinse well with a solution that will remove the entire sample from the bulb. In the case of alcohol samples, a simple water rinse is sufficient.

Blot oily or greasy samples from the bulb and the junction with a lint-free wiper. Consider rinsing with a detergent solution, followed by water.

In the case of other non-aqueous samples that do not mix with water, use an intermediate rinse solution, which mixes both with water and with the sample. An alcohol or the titration solvent may be suitable. Then rinse with water. Rinse again with the intermediate rinse solution before putting the electrode into the next sample. Remove the pH electrode from the sample and rinse it as soon as the measurement is done.

Be aware that aqueous buffers may not accurately calibrate pH for non-aqueous or mixed sample testing. In general, the concept of pH becomes a relative measurement in these samples.

There are alternate buffers available, such as water-methanol and water-ethanol buffer systems as described by IUPAC[6].

A titration for acidity or basicity, rather than a pH measurement, may be appropriate for non-aqueous samples. The Orion 8172BNWP pH electrode is our recommendation for manual and automatic titrations for these types of samples.

Due to the effects of the sample on the pH electrode, slower response and some drift is expected. Use stirring to speed the response. One option is to allow extra time for the electrode to reach a stable reading. Alternately, use a consistent, timed reading. For example, ASTM D6423 for ethanol/biofuels specifies that each reading be taken at 30 seconds after immersing in sample.

Conclusion

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

References

[1] ASTM D664, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. www.astm.org.

[2] ASTM D2896, Standard Test Method for Base Number of Petroleum Products by Potentiometric Perchloric Acid Titration. www.astm.org.

[3] ASTM D6423, Standard Test Method for Determination of pHe of Ethanol, Denatured Fuel Ethanol, and Fuel Ethanol. www.astm.org.

[4] ASTM D4980, Standard Test Method for Screening of pH in Waste, www.astm.org.

[5] C. Clark Westcott, pH Measurements. Academic Press, New York, USA. 1978. P, 113.

[6] Mussini, P.R. et al, Reference Value Standards and Primary Standards for pH Measurements in D2O and Aqueous-Organic Solvent Mixtures: New Accessions and Assessments. Pure & Applied Chemistry, Vol. 69, No. 5, pp. 1007-1014, 1997.

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
Electrodes	Thermo Scientific Orion ROSS Sure-Flow pH Electrode	8172BNWP
Solutions	Thermo Scientific™ Orion™ pH Electrode Cleaning Solution D	900024
	Thermo Scientific Orion General Purpose pH Electrode Cleaning Solution C	900023
Meters	Thermo Scientific Orion VERSA STAR Multi-parameter Benchtop Meter	VSTAR93
	Thermo Scientific Orion VERSA STAR pH/LogR Benchtop Meter Kit	VSTAR82
	Thermo Scientific Orion VERSA STAR pH Benchtop Meter	VSTAR10

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