APPLICATION NOTE

pHe of ethanol fuel

Water Analysis Instruments, Thermo Fisher Scientific

Key Words
pH, pHe, ethanol, fuel, ASTM D6423, denatured fuel ethanol, ethanol fuel blends, acid strength, corrosion potential, 8172, Star A211, pH benchtop meter

Goal

This application note utilizes a Thermo Scientific™ Orion™ pH benchtop meter and Thermo Scientific™ Orion™ ROSS™ Sure-Flow™ 8172BNWP pH electrode to measure pHe in Fuel Ethanol. In addition, tips for optimal performance are included at the end of this note.

Introduction

This application note covers a procedure to determine a measure of the acid strength of ethanol fuel. According to the ASTM D6423 Standard, the acid strength of ethanol fuels is defined as pHe. According to ASTM D6423[1], the Orion ROSS Sure-Flow pH electrode with glass body can be used for determination of pHe in ethanol fuel. The special features of the Orion 8172BNWP electrode, such as the low resistance glass membrane, sure-flow junction, and glass body resistant to chemical attack, guarantee precise measurement and good accuracy of pHe measurements.

Recommended Equipment

- Thermo Scientific™ Orion Star™ A-Series benchtop meter, or Thermo Scientific™ Orion™ Dual Star™ meter, or Thermo Scientific™ Orion™ Versa Star Pro™ meter
- Orion ROSS Sure-Flow pH Electrode (Cat. No. 8172BNWP)
- Orion ATC probe (Cat. No. 927007MD)
- Stirrer (Cat. No. 096019)
- Timer

Optional:

- RS232 computer interface cable (Cat. No. 1010053)

Required Solutions

- Orion pH 4.01 and 7.00 buffers (Cat. No. 910104, 910107)
- Filling solution (Cat. No. 810007)
- Orion storage solution (Cat. No. 810001) or Orion pH electrode storage solution (Cat. No. 910001)
- Laboratory Reagent Water (LRW)
- 1 N hydrochloric acid
- 1 N sodium hydroxide

Solutions Preparation

Prepare 1 N Hydrochloric acid by dissolving 42 mL of concentrated HCl in 500 mL volumetric flask with LRW or purchase from a commercial source. Prepare 1 N sodium hydroxide by dissolving 20 g NaOH in 500 mL volumetric flask with LRW or purchase from a commercial source.

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Meter Setup

Connect the pH electrode and the ATC sensor to the meter. Connect stirrer to the meter. Set measurement mode to pH. In Setup mode, set resolution to 0.01, buffer set to USA and read type to continuous. If the ATC is connected properly, the true temperature (not the reference 25.0) will be displayed on the screen. Set stirrer speed to 3.

Electrode Setup

See the electrode user guide for preparation of the electrode.

Electrode Performance Check

Check slope (see Calibration section) and drift. Drift may be checked by comparing a 1-minute to 2-minute reading.

Results should agree with desired criteria. See troubleshooting section of user guide if slope and/or drift are not acceptable. Be sure electrode is working properly before taking measurements.

Electrode Cleaning and Rehydration

The electrode should be cleaned and/or rehydrated before tests and between readings. The cleaning/rehydration procedure is a necessary step to preserve the electrode's performance characteristics. Follow these steps to ensure that the electrode sensing bulb and reference junction are fully hydrated:

- Before testing the alcohol fuel samples and after every 10 samples, clean and rehydrate the electrode by alternately soaking in 1 N HCL, 1 N NaOH, and 1 N HCl for 30 seconds in each; then soak in pH electrode storage solution for 5 minutes. Before placing in each solution, rinse the electrode with LRW.
- Between each sample measurement, rehydrate by soaking the electrode in pH 7 buffer for at least 20 seconds or until the pH value falls below 7.05.

Sample Preservation

None required.

Sample Preparation

Measure 50 mL of sample into a 100 mL beaker.

Calibration

See meter user guide for calibration procedure directions. Perform two point calibration using pH 4.01 and 7.00 buffers. The calibration and measurement should be done at 20 ±2 ºC. The electrode slope should be between 95 - 100%. If the slope is not within that range, perform electrode maintenance and/or use fresh buffer solution. Repeat the calibration until satisfactory results. Check calibration by reading pH buffer(s).

Analysis

Rinse the pH electrode, ATC probe, and stirrer with LRW. Place probe in the sample and turn on the stirrer. Start the timer. After exactly 30 seconds, record the reading. Remove electrode from ethanol immediately. To avoid ethanol fuel evaporation and dehydration of sensing bulb, rinse the electrode immediately with LRW and place in the pH 7 buffer for at least 20 seconds and until the reading is less than pH 7.05. Before measuring the next sample, rinse the electrode with LRW.

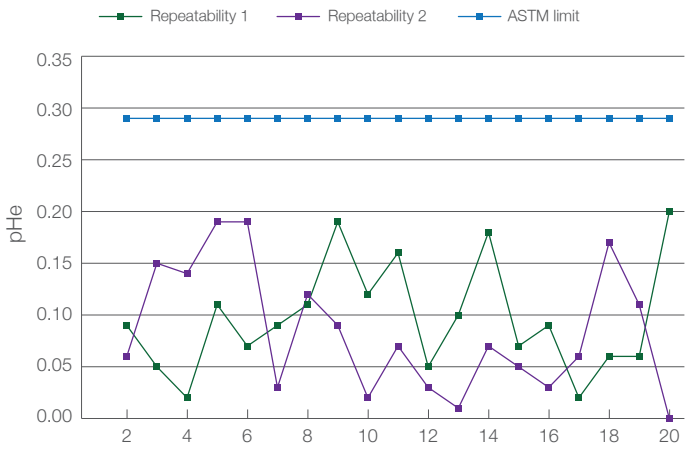
Quality Control (QC)

Recommended QC procedures include: calibration and calibration verification, sample duplicates, slope, drift, and between-measurement pH 7 checks.

Results and Performance

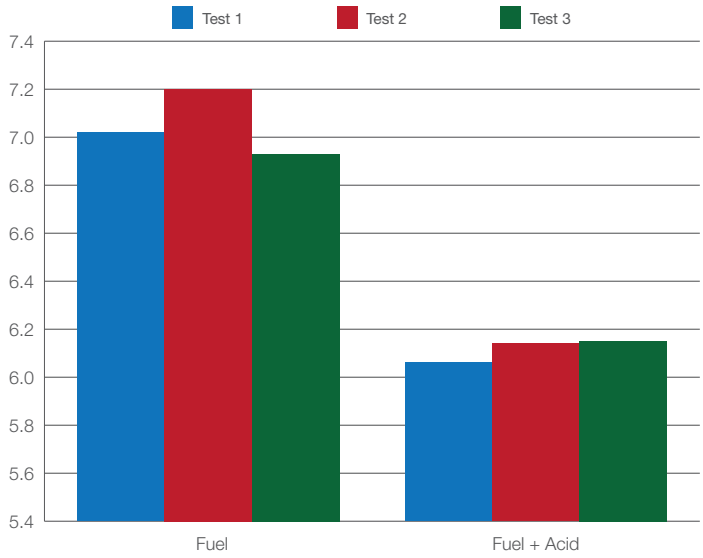
An ethanol fuel sample was tested twenty times by two Orion 8172BNWP pH electrodes to demonstrate the repeatability and performance of the pH meter and electrode. Results are shown in the table and graph below

Repeatability (moving range) of 20 identical ethanol/gasoline samples measured by two Orion ROSS 8172 Sure-Flow electrodes



As shown on the chart above, the repeatability of successive measurements of twenty ethanol fuel samples by the Orion 8172BNWP electrode is in accordance with the ASTM D 6423-08 Standard; the biggest deviation between successive results is 0.29 pHe or less.

Testing fuel and acidified fuel



When cycling between fuel and acidified fuel, the Orion ROSS Sure-Flow electrode showed good repeatability and was sensitive to the acid additive.

Tips for Optimal Performance

Electrode cleaning/rehydration before use and after every ten samples

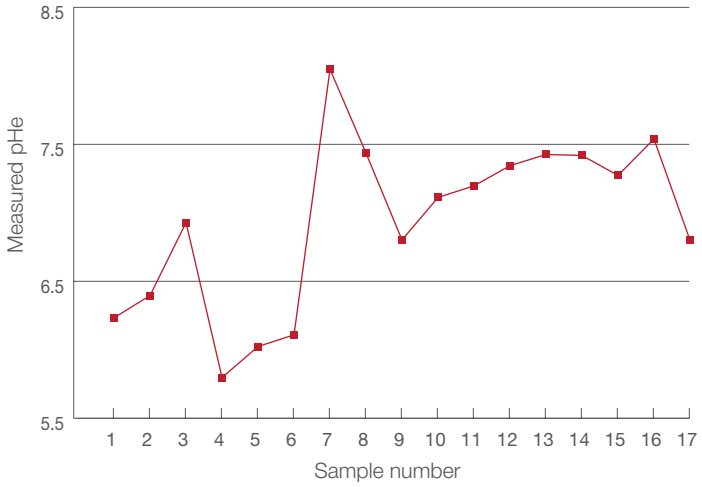
ASTM D 6423 suggests that before first use in alcohol fuel solutions and after every ten samples, clean/rehydrate the electrode by alternately soaking several times in 1 N NaOH solution and 1 N H_2SO_4 (or 1 N HCl) for about 30 seconds each.

We used and modified this recommendation slightly to clean and rehydrate the electrode as follows:

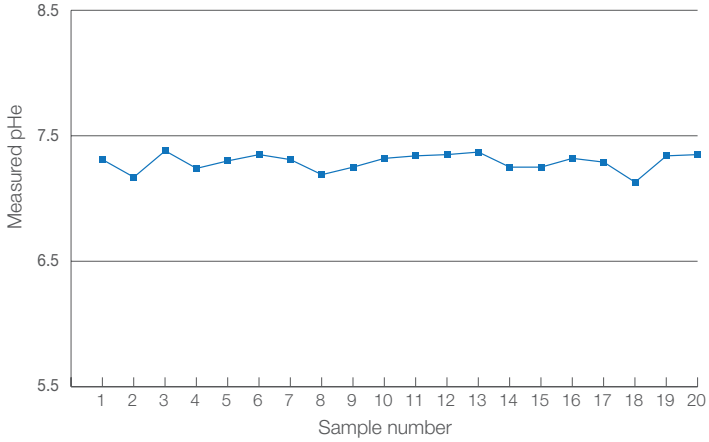
- 30 seconds in 1 N HCl, rinse with DI water
- 30 seconds in 1 N NaOH, rinse with DI water
- 30 seconds in 1 N HCl, rinse with DI water
- 5 minutes soak in pH electrode storage solution (Orion 910001 or 810001), rinse with DI water

The following charts are an example of pHe tests before and after applying cleaning/rehydration procedure. The cleaning/rehydration step improves the precision of the electrode and is a valuable step.

pHe readings before cleaning/rehydrating procedure



pHe readings after cleaning/rehydrating procedure

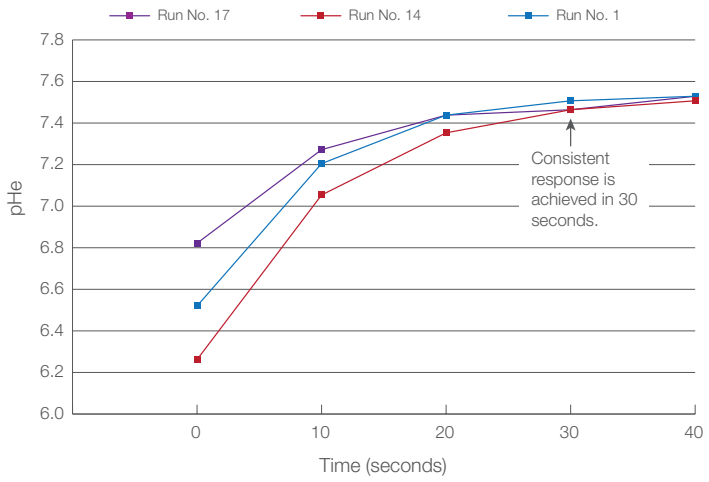


Measure the pHe at Exactly 30 ±1 Second

The ASTM standard requires that the readings be taken at exactly 30 seconds.

We found that 30 seconds is enough time for a fast electrode to respond and is a short enough time to avoid significant dehydration of the electrode (which would cause unresponsiveness to hydrogen ions). Immediately after each measurement, remove the electrode from the ethanol to avoid further dehydration of the glass bulb.

Examples of pHe response of 8172 in fuel ethanol blend



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Rinse the Electrode Immediately

After removing the electrode from the ethanol sample, rinse immediately. The immediate rinse will avoid ethanol evaporation from the bulb and the associated cooling and dehydration. For best results, don't allow ethanol evaporation from the bulb.

Electrode Rehydration Between Sample Measurements

When soaking electrodes between sample measurements in pH 7, we observed that both electrodes stabilized quickly and reached a value below 7.05 in less than 20 seconds, as required by ASTM D6423. Note that the pH at 20 seconds is always within ±0.03 pH of pH 7.00. Due to this performance, the testing proceeded quickly, and the electrode did not need recalibration during testing.

pH 7 buffer readings during pHe testing

	Elect. 1	Elect. 2
Average pH	6.98	7.01
STDEV	0.008	0.011

Conclusion

Apps Lab applied these techniques for pHe testing of multiple ethanol fuel samples with the Orion ROSS Sure-Flow electrodes and obtained outstanding results. The results in this Application Note demonstrate that the precision and repeatability limits for the Orion ROSS Sure-Flow electrodes are better than reported in the ASTM D 6423 Standard.

Reference

[1]ASTM International, D6423-08, Standard Test Method for Determination of pHe of ethanol, denatured fuel ethanol, and fuel ethanol.

To purchase Thermo Scientific laboratory products, please contact your local equipment distributor and reference the part numbers listed below:

Product	Description	Cat. No.
Meters	Thermo Scientific Orion A211 pH benchtop meter	STARA2110
	Thermo Scientific Orion pH/ISE meter	2115000
	Thermo Scientific Orion Versa Star Pro pH benchtop meter	VSTAR10
Electrodes	Thermo Scientific Orion ROSS Sure-Flow pH Electrode	8172BNWP
	Thermo Scientific Orion ATC probe	927007MD
Solutions	Thermo Scientific Orion pH 4.01 buffer	910104
	Thermo Scientific Orion pH 7.00 buffer	910107
	Filling solution	810007
Accessories	Stirrer	096019
Laboratory Reagent Water	Thermo Scientific Barnstead Smart2Pure 12 UV Water Purification System	50129890*

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