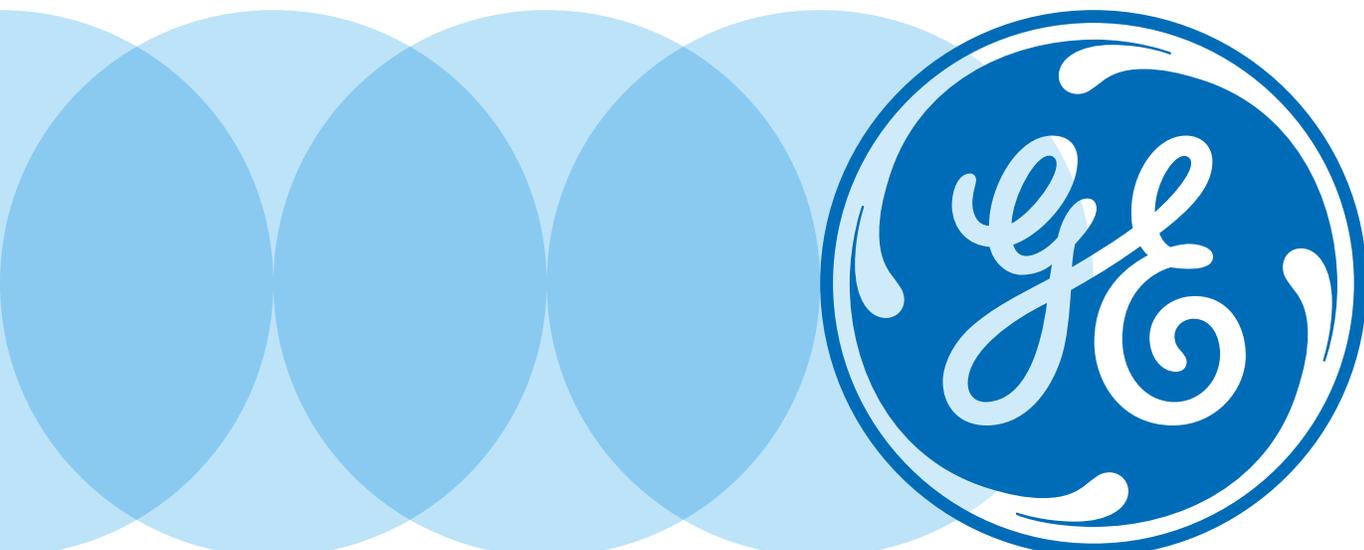


Aurora TDLAS analyzers for Hydrogen Recycle Applications

Technical White Paper

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1. Introduction

The objective of the petroleum refining process is to convert crude oil into useful and profitable end products such as gasoline, jet fuel, diesel oil, liquefied petroleum gas and fuel oils. Hydrogen is widely used in these downstream refining processes for the following reasons:

- increase the efficiency or throughput of the chemical reaction,
- optimize the yield of the desired end product,
- improve quality of end product,
- remove undesired contaminants in fuels, such as sulfur, and
- maximize catalyst life

Clean fuels regulations are being implemented in many parts of the world including Europe and the USA, and are going to become stricter as time progresses. Major oil refinery upgrades are necessary in order to meet these specifications, and one of the consequences is that hydrogen demand will increase dramatically. Various sub-processes used in refining include hydro-treating, hydrocracking, catalytic reforming, isomerization, alkylation and several others. These sub-processes vary depending on the input feed stock and the desired modification to that feed stock. Process objectives include conversion of petroleum refinery naphthas distilled from crude oil (typically having low octane ratings) into high-octane liquid reformates, sulfur removal, and producing specific end products, such as diesel oil.

It is estimated that the total hydrogen consumption in oil refineries is 12.4 BCF/day or approximately 100-200 SCF/bbl of oil processed. Hydrogen consumption is growing at 5–10% CAGR driven by low sulfur in diesel fuel requirements, increasing use of low quality heavy crude oil, which requires more hydrogen to refine, and increased global oil consumption driven by emerging markets such as China and India. Therefore, management of hydrogen and its associated cost is critical to the profitability of refineries [1].

The moisture content in H₂ recycle processes can vary from the sub-part per million by volume (PPMv) level to higher concentration of ~20 – 30 PPMv. For example, in isomerization, the moisture content must be tightly controlled to less than 1 PPMv to prevent poisoning of the Pt/metal oxide catalysts due to hydrogen removal, consequently reducing catalyst lifetime and driving up costs. For catalytic reforming of crude oil, moisture is a necessary component of the reaction chemistry and must be maintained at the 15–20 PPMv level [2].

2. Online Moisture Measurement for Catalytic Reformer Units

The efficiency of producing desired chemical reactions, and therefore, output yield of the required petroleum products is adversely affected if moisture content in the recycle gas is not maintained in the optimum range 20 to 30 PPMv. Hydrocarbon crackers incur significant cost from inaccurate and slow responding online moisture sensors. Current technology utilized to monitor moisture levels in hydrogen recycle gas mixtures includes Quartz crystal microbalance (QCM) analyzers and Aluminum Oxide based probes. These methods have several drawbacks that can delay the moisture measurement, resulting in process excursions and off-specification product. QCM technology requires the sensor to be continually compared with a reference “zero” gas, which results in a non-continuous measurement. The self-verification requires the ability to generate a known moisture content using a desiccant, permeation tube and precise gas flow rates. As such, a QCM analyzer has a fairly complex internal sample handling system increasing the CAPEX and requiring significant maintenance, which increases OPEX as well. Aluminum oxide sensors are generally slower responding to very dry gas and can drift over time [3].

While Tunable Diode Laser Absorption Spectroscopy (TDLAS) provides fast and accurate analyzers with a higher initial cost compared to other technologies, the return on investment is achieved by speed of response, reliability, repeatability, and negligible maintenance requirements (i.e., recalibration and replacement of moisture probes). Maintenance requirements include cost of

uninstalling, replacing the probe, shipment to a service center, calibration fees, return shipment to the site and reinstallation. QCM analyzers require replacement of the desiccant and maintenance to the internal sample system periodically. The recommended cycle for recalibrating Aluminum Oxide sensors is 6 – 12 months, while TDLAS has no required factory service.

During “turnarounds” or process upsets, TDLAS technology has been proven to provide the fastest response and recovery once the process upset is corrected or dissipates, and to run for years without the need of any major maintenance or recalibration [4]. Key advantages of TDLAS include:

- Fast real-time measurement with no wet up or dry-down delays – responds to changes in H₂O concentration in the process gas in seconds
- Virtually maintenance free with no routine field calibration and/or expensive consumable requirements
- Non-contact continuous moisture measurement with no damage to critical sensor components (tunable diode laser and detection optics) from HCl and other contaminants in the process by sample conditioning to isolate them from the process gas
- Sample conditioning and reduced pressure high-resolution spectroscopy (Aurora Trace) can minimize interference to moisture measurement from other compounds in the process gas

3. Aurora TDLAS platform

GE’s Aurora analyzer employs TDLAS to rapidly and accurately measure moisture content in a variety of background gases including N₂, H₂, CO₂, and hydrocarbons. This analyzer is suitable for installation in hazardous areas and operates over a wide range of environmental conditions. We present below key performance attributes of the Aurora moisture analyzer for use in online measurement of the H2 recycle stream in various types of downstream refining processes.

The Aurora H₂O is the base model wherein a single-pass absorption cell operates at atmospheric pressure to provide a lower detection limit of 5 PPMv. It uses a near-infrared diode laser rapidly tuned over a narrow band of optical frequencies that includes the molecular absorption peak of H₂O to directly measure the partial pressure of water vapor in the background gas [5]. With the simultaneous measurement of sample pressure and temperature, the Aurora generates the following moisture content readings simultaneously at a rate of ~5 per second:

- Molar volume ratio in parts per million by volume (PPMv)
- Absolute humidity in pounds per million standard cubic feet (lbs/mm scf) or milligrams per cubic meter (mg/m³)
- Saturation temperature of Dew point/Frost point in °C or °F
- Equivalent dew point at line pressure in °C or °F

Table 1: Detailed performance specifications for Aurora TDLAS high-precision moisture analyzers as relevant to the H2 recycle downstream applications.

PARAMETER	AURORA H ₂ O SPECIFICATION
RANGE	
Calibrated range	0 to 5000 PPMv
Lower Detection Level	5 PPMv
Dew/Frost Point	-85.9° to 27.3°F (-65.5° to -2.6°C) frost point @ STP of 25°C, 14.696 psia
ACCURACY	
Parts Per Million by Volume	±2% of reading or 4 PPMv at nominal gas composition with up to 5% variation in H ₂ and 1% variation in C ₂ H ₆ from nominal gas composition

Repeatability	±2 PPBv (parts per billion by volume) below 200 ppm; 1% above 200 ppm
RESPONSE TIME	
Response Time	Optical system < 2 seconds
System response	The system response is dependent on the length of sample tubing, sample system components, flow rate and pressure, as well as the change in moisture concentration.
HAZARDOUS AREA CERTIFICATION	
USA/Canada	Explosion-proof for Class I, Division 1, Groups B, C, and D
EU and Elsewhere	ATEX and IEC Ex: Ex de IIB + H2 T6 -20°C to +65°C; Flameproof with increased safety compartment

4. Aurora H₂O Performance in H₂ Recycle Process Stream

Three critical performance metrics for the fast response Aurora H₂O analyzer are its accuracy, stability and speed of response. Figure 1 below demonstrates the performance of an Aurora H₂O unit that has been calibrated on a precision dew-point generator in a custom hydrocarbon mix representative of the H₂ recycle process over the 5 – 5000 PPMv range of moisture. A “typical” process gas mix of 80 mole% H₂, 10 mole% CH₄, and 10 mole% C₂H₆ representative of H₂ recycle moisture monitoring applications was used. Besides Hydrogen, it includes the two background components (Methane and Ethane) that have the greatest effect on H₂O reading accuracy.

The gas mixtures used in this calibration and verification is provided by blending high-purity gases through a flow manifold with digital mass-flow controllers (MFC) that have ±1% uncertainty in the actual flow. The H₂O vapor content in the gas mix at the outlet of this moisture generator is controlled by variable dilution of dry gas with wet gas delivered from a membrane-based isothermal saturator, and is determined by precise control of flow, pressure, and temperature. A GE Optica 1311-XR fast-response chilled mirror serves as a NIST traceable reference for moisture measurements in all laboratory testing.

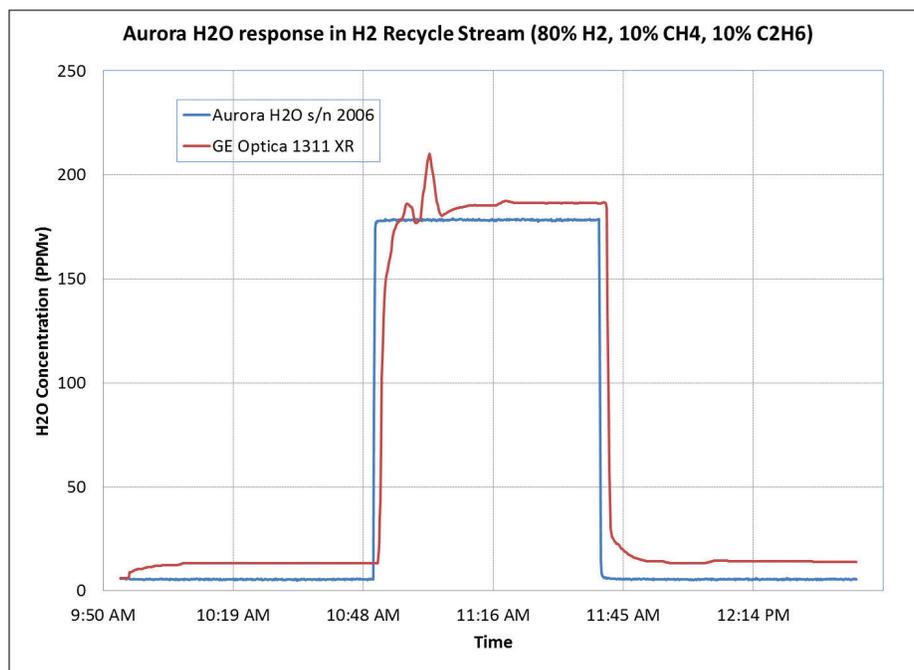


Figure 1: Performance of Aurora H₂O unit over a range of moisture concentration in H₂ recycle process stream (80% H₂, 10% CH₄, and 10% C₂H₆) illustrating accuracy of calibration, stability and speed of response.

As shown in Figure 1, the H₂O analyzer reading changes in <10 seconds and stabilizes both during wet-up and dry-down almost instantly with an undetectable overshoot. The standard deviation of the H₂O reading is $\sigma < 0.25$ PPMv over 1 hour as compared to $\sigma > 25$ PPMv for the chilled mirror hygrometer. The analyzer's moisture reading deviates from the reference by less than its $\pm 2\%$ or 4 PPMv accuracy spec (after factoring in the ± 4 PPMv accuracy of the chilled mirror hygrometer) at both the low end (5 PPMv) and the high end (~175 PPMv) of dew point used in this test.

A similar moisture accuracy verification test has been conducted on the calibrated Aurora H₂O analyzer to demonstrate the accuracy of its moisture reading over a range of variation in the background gas composition. Table 2 below shows the results of this test over the following range of background gas variation (calibration mix is 80% H₂, 10% CH₄, and 10% C₂H₆):

- Hydrogen 80 \pm 5 mole %
- Methane 10 \pm 5 mole %
- Ethane 10 \pm 5 mole %

This test was performed at a low moisture level of ~10 PPMv and a high moisture level of ~100 PPMv, with a minimum 30-minute dwell time for the analyzer in each composition. The accuracy specification of the Aurora H₂O analyzer for H₂ recycle applications is $\pm 2\%$ or 4 PPMv (whichever is greater) for up to $\pm 5\%$ variation in H₂ content or $\pm 1\%$ variation in C₂H₆ content vis-à-vis the nominal calibration mix. The overall error tolerance in this test is ± 5.66 PPMv, which is the Root Sum of Squares of the specified ± 4 PPMv accuracy of the H₂O analyzer and the specified ± 4 PPMv accuracy of reference chilled mirror hygrometer.

Table 2: Accuracy of moisture readings from Aurora H₂O analyzer over a range of variation of process gas composition

Verification Gas Mixture (mole %)			H ₂ O reading (PPMv)	Reference reading (PPMv)	Error (PPMv)
H ₂	CH ₄	C ₂ H ₆			
80	10	10	96.63	96.65	-0.02
80	5	15	102.12	96.91	5.21
80	15	5	90.77	96.80	-6.03
80	10	10	97.13	98.02	-0.89
85	10	5	92.70	97.39	-4.69
75	10	15	100.96	98.15	2.81
80	10	10	97.57	98.62	-1.04
85	5	10	96.11	99.68	-3.57
75	15	10	99.72	99.42	0.30
80	10	10	11.02	13.69	-2.68
80	5	15	17.12	13.62	3.50
80	15	5	4.47	13.53	-9.07
80	10	10	11.12	13.49	-2.37
85	10	5	6.09	13.49	-7.40
75	10	15	15.29	13.77	1.53
80	10	10	11.96	13.47	-1.51
85	5	10	10.27	13.51	-3.24
75	15	10	13.80	13.50	0.31

Figure 2 and Figure 3 below illustrate the dependence of the observed errors in the measured moisture concentration as a function of the background Hydrogen and Ethane content respectively. Horizontal dashed green lines indicate the Upper and Lower Spec Limits for the overall error in this test. Vertical green lines indicate the allowed range of variation in background gas composition over which the analyzer is designed to stay within spec.

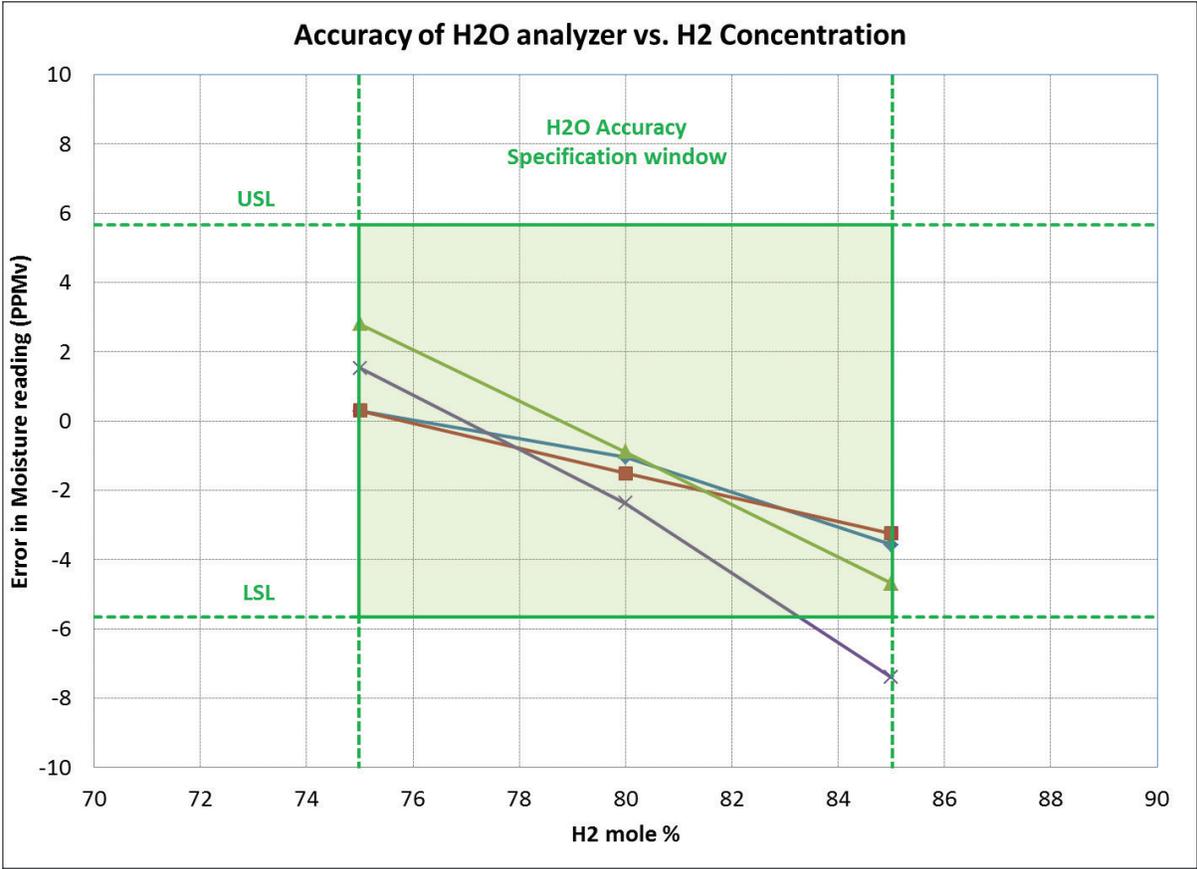


Figure 2: Variation of Aurora H₂O accuracy with background gas Hydrogen content showing the analyzer is within its accuracy specification. The only outlier is for the case wherein the change in the C₂H₆ level is outside the specified ±1% range.

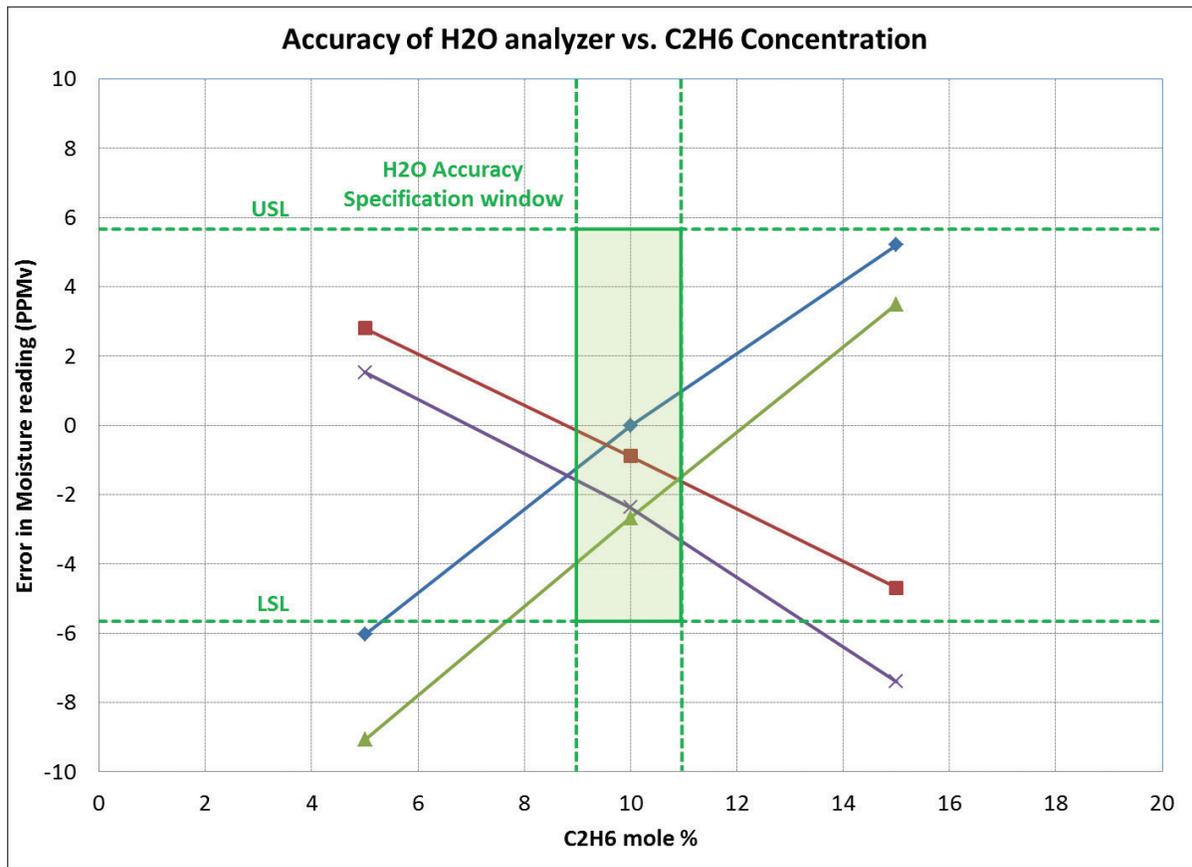


Figure 3: Variation of Aurora H₂O accuracy with background gas Ethane content showing the Analyzer is within spec within the ±1% range of variation.

As is evident from these plots and Table 1, the H₂O analyzer meets its accuracy specification over the ±5% variation in H₂ content or ±1% variation in C₂H₆ content. These data lead to the following conclusions:

1. All the errors are purely OFFSET errors, i.e., the difference between the H₂O and reference readings is NOT a function of the moisture level. This is as expected from the system response model calculations that account for spectral interference between H₂O, CH₄ and C₂H₆.
2. There are clear monotonic trends in analyzer error with changes in H₂ and C₂H₆ content. Hence, these data can potentially be used to develop a unit-specific offset to compensate for a known change in the background gas composition during calibration.
3. The change in the H₂O reading with respect to that in the nominal mix is the highest for a 1% change in the C₂H₆ level, and the lowest for a 1% change in H₂.

References:

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