

HCR (Hydrocarbon Resistant) Fiber Optic Oxygen Sensor

Technical Note

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5/19/2013

- **Summary:**
 - Hydrocarbon resistant (HCR) fiber optic dissolved oxygen (DO) sensor is used to monitor DO in kerosene liquid. HCR optical sensor is based on luminescence dynamic quenching of molecular probe by oxygen molecules. The compatibility, sensitivity and stability of the HCR oxygen sensor when immersed in kerosene are demonstrated. Kerosene is used as a representative media because it contains both aromatic and aliphatic hydrocarbons. Some of the critical properties of HCR oxygen sensor are determined including long term stability in hydrocarbon based fuel, thermal cycling stability, response rate and response to oxygen variation in fuel.
- **Significance:**
 - The significance of HCR optical oxygen sensor is the compatibility of the sensor with pure organic solvents and hydrocarbon based fuels. To our knowledge no other product exists in the market that can survive in such environments.
 - The other factor of significance is the stability of the sensor. The sensor has shown small drift due to photobleaching and/or environmental effects when used in hydrocarbon based fuels. To our knowledge no other product exists worldwide that has come close to exhibiting these properties.
- **Background:**
 - **Why it is important to monitor oxygen in hydrocarbons:** Monitoring oxygen content of hydrocarbon stream is important for several reasons. When the oxygen molecules dissolved in hydrocarbon combine with other chemical and/ or biological species within the hydrocarbon stream, this may cause fouling and corrosion within the stream and also to the equipment used for handling the hydrocarbon stream. The oxygen measurement may also be used to determine the efficiency of oxygen scavengers for adjusting the dosage of the oxygen scavengers.

- **Types of hydrocarbons:** The hydrocarbon stream may be or include, but is not limited to, a mixed C4 hydrocarbon stream, a light ends hydrocarbon stream, a styrene hydrocarbon stream, a refinery fluid, cracked gas distillates, hydrotreater feeds, kerosene, a pyrolysis gas stream, and combinations thereof
- **Prior art:** Prior art methods for determining dissolved oxygen concentration in liquid fuel and hydrocarbon process streams are cumbersome and time consuming as to be rendered substantially useless for many measurements. For example, methods based on gas chromatography (GC) and combined GC and mass spectrometry (MS) are sensitive to at least a few parts per million (ppm) O₂ and give results with fairly high precision. However, in the GC based method, the oxygen must be separated from the hydrocarbon prior to introduction to the GC column. Any hydrocarbon in the GC sample also degrades column efficiency, so the column must be run through a heating cycle regularly to remove small amounts of and hydrocarbon process streams. GC does not allow study of rapidly time-varying signals and is performed off-line, which prevents in-situ and spatially resolved sample measurements. Moreover, these methods are expensive to perform.

Electrochemical methods, such as potentiometry and voltammetry, may be used for analysis of oxygen species. Oxygen is detectable with high sensitivity by polarography in aviation fuel because of a paucity of other reducible species in the fuel, but the interface between the fuel and the electrochemical cell is cumbersome and the measurement is slow and cannot be performed non-invasively.

Oxygen is difficult to measure spectroscopically in organic solutions because O₂ does not absorb in the infrared and has electronic transitions in the far ultraviolet spectrum where organic solutions strongly absorb. Although it has a Raman allowed transition and unique electron spin resonance, methods based on these attributes have low sensitivity, high cost and experimental complexity.

- Report:
 - **Sensor performance in Kerosene fuel:** We tested the sensor in kerosene at zero oxygen (by saturation with nitrogen) and saturation with air. Figure 1 shows the sample response to oxygen in kerosene at room temperature.

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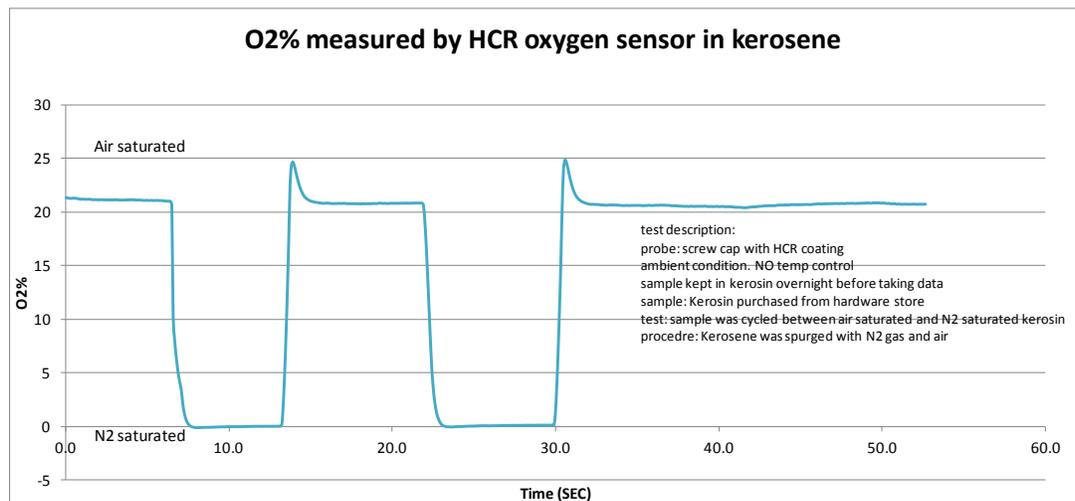


Figure 1

- **Sensor short term stability in kerosene:** A HCR probe was immersed in kerosene for 24 hours. During that time the sensor's raw data and oxygen readings were monitored. Temperature was kept constant by placing the sample in a water bath at 26 C. As shown in Figures 2 and 3 the sensor showed excellent stability with no drift during the 24 hours of testing. There were some minor fluctuations due to temperature variations as shown in Figure 2. Figure 2 shows the sensor's raw data and Figure 3 shows the sensor's O2 readings without temperature compensation.

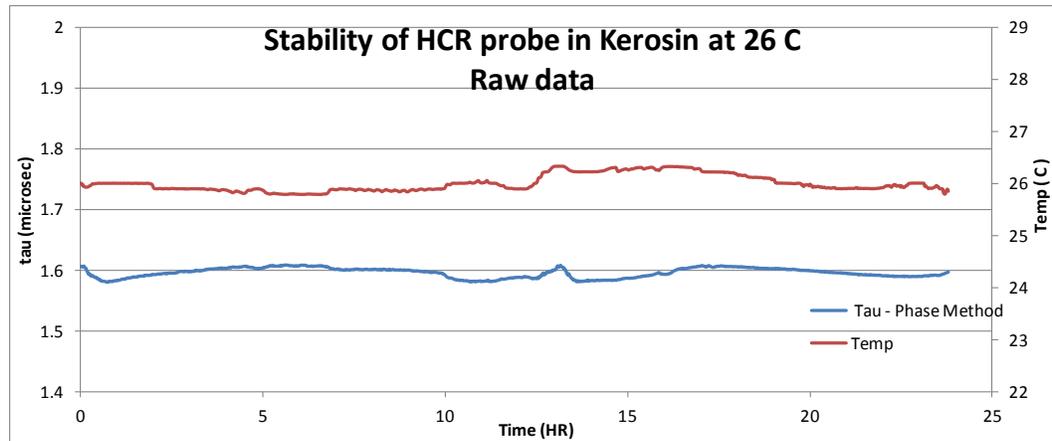


Figure 2

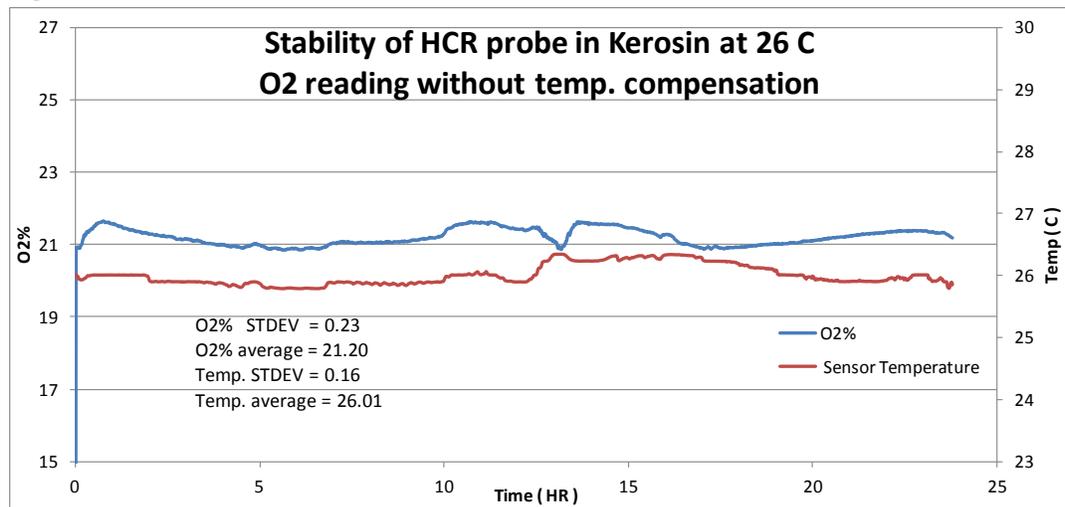


Figure 3

- **Sensor response to heat cycle:** The sensor's response to oxygen was monitored before and after heating the sensor at 80 C for 24 and for 48 hours in air. Table 1 shows the tau values in N2 (0% O2) and air (20.9% O2), and the corresponding temperatures before and after heat treatments. R factor is also shown in table 1.

Effect of Heating on HCR sensor					
	status	tau0	Tau(air)	R(tau0/tauair)	T (C)
	befor	2.12	1.49	1.42	26.65
	after 24 HRS heat	2.19	1.51	1.45	26.85
	after 48 HRS heat	2.19	1.56	1.41	26.35

Table 1

As shown in table 1, R factor as well as individual tau values are changing slightly with temperature as expected. No other noticeable changes were seen in sensor response after heat treatment.

- **Sensor response rate in gas:** Sensor response rate in gas was determined to be 1 second at 90% equilibrium as shown in Figure 4. Response rate was determined by monitoring the time it takes for the sensor to establish equilibrium when switched from N2 flow to air flow. The response rate determined in this test is for a dip coated probe. For spin coated probes such as screw cap and patches, the response time will be faster than 1 second.

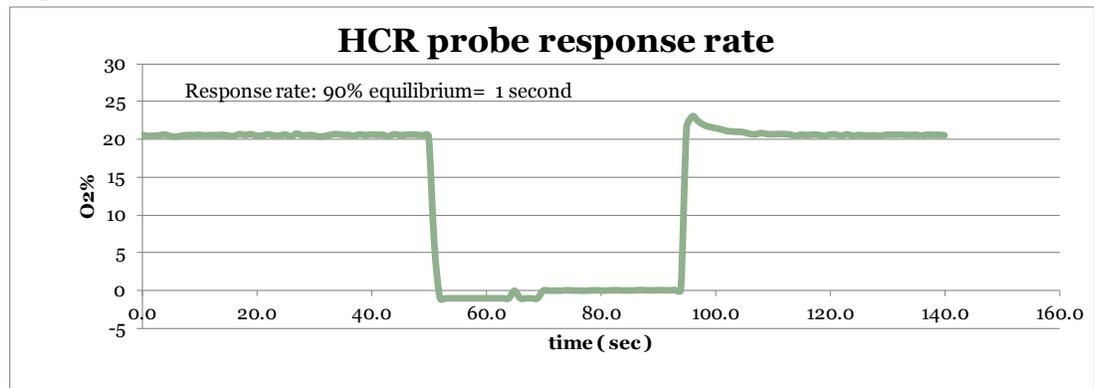


Figure 4

- **Sensor long term response:** sensor was placed in kerosene for 51 days at ambient condition. Kerosene was purged with nitrogen gas and air frequently. Sensor signal (tau) was monitored when kerosene was saturated with nitrogen (0% oxygen) and with air (20.9% oxygen). R factor which is tau in nitrogen/tau in

air was also calculated and plotted. R factor represents sensor calibration slope. Figure 5 shows sensor response during 51 days. It appears that during 1st 2 weeks there was some drift and then stabilized. This data suggest that sensor calibration needs to be reset from time to time using single point calibration reset. In single point calibration reset, sensor is purged with a known gas (i.e. air or nitrogen) and calibration intercept is reset.

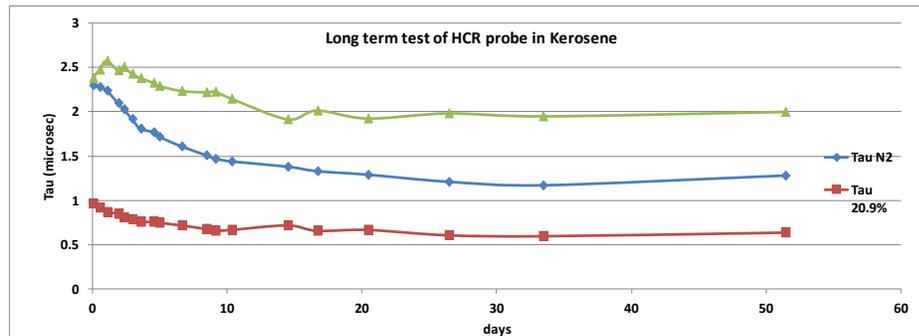


Figure 5. Sensor long term response in kerosene