PetroSense® Hydrocarbon Sensors and Their Applications

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Introduction

The increasing concern about hydrocarbon contamination of process water and produced water has created an increasing need for in-situ, real time, and accurate low cost instrumentation that can provide rapid detection and easily usable in the field.

PetroSense® sensors [1,2] represents "best in breed" technology for the detection of total petroleum hydrocarbons (TPH). PetroSense® sensors are incorporated in both a portable, field screening instrument (the PHA-100) and a continuous monitoring system (the CMS-4000). These sensors utilize fiber optic systems and are designed for in-situ, real time measurements of TPH and other related pollutants.

PetroSense® sensors operate in air (vapor), water and soil. PetroSense® sensors are non-specific detectors for TPH, semi-volatile hydrocarbons (e.g., diesel fuel, heating fuels, etc.), trichloroethylene/perchloroethylene and many other related compounds. The detection capability of these sensors is unaffected by high humidity, or by naturally occurring methane. PetroSense® sensors have been used in a variety of applications:

In-situ vapor measurements in wells
In-situ water measurements in wells
Cooling Tower monitoring
Water measurements in bailed samples from wells
Surface water measurements
Tracking of a hydrocarbon leak in progress (plume migration)
In-situ monitor for vapor extraction systems
Leak detection for above ground and underground storage tanks
Leak detection for pipelines
Storm water runoff monitoring
Sample screening for laboratory analyses
Site assessment
Groundwater remediation

Although these sensors are non-specific, there is a relative response characteristic for the different compounds that are detected. The PetroSense® sensors have a very strong response for aromatic and other large hydrocarbon compounds. This makes these sensors very useful for the detection of BTEX (benzene, toluene, ethyl benzene and xylenes), which is used as a tracer for TPH leaks/contamination. The characteristic relative response factors (RRF's) can be determined for specific sites. The sensors can be calibrated for specific compounds expected at a given site, or the non-specific readings can be converted to the concentrations of these specific compounds by use of the appropriate RRF's.

PetroSense® Hydrocarbon Sensor Technology

PetroSense® sensors [1] represent the "best in breed" technology for the detection of total petroleum hydrocarbons (TPH). PetroSense® sensors are incorporated in both a portable, field screening instrument (the PHA-100plus) and a continuous monitoring system (CMS-5000) [2] for the monitoring of vapor and dissolved hydrocarbons in water. These sensors utilize fiber optic systems and are designed for in-situ, real-time measurements of TPH and other related pollutants.

The principle behind the PetroSense® technology is the modulation of light guided along an optical fiber. Optical fibers are utilized for the transmission of light based upon the phenomenon of total internal reflection.

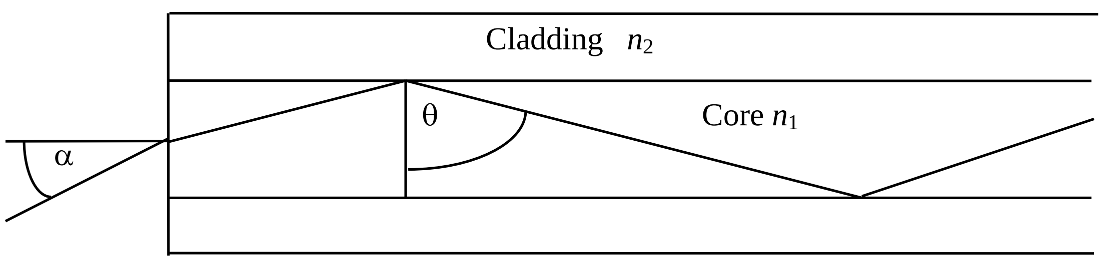


Figure 1. Schematic of an optical fiber: α is the acceptance angle; n_1 and n_2 are the refractive indices.

Light entering the end of a fiber optic is completely reflected within the fiber and therefore transmitted through the fiber, if it strikes the core of the fiber with an incident angle greater than a characteristic critical angle θ. This critical angle is determined by the refractive indices (n) of the glass and the surrounding medium. By cladding the fiber optic core with materials with certain refractive indices, the amount of internally reflected light can be optimized. The relationship of this critical angle and the refractive indices can be approximated by the following equation based upon the half-angle of the incident light, α:

$$\sin\alpha = \frac{(n_1^2 - n_2^2)^{1/2}}{n_0}$$

When the outer medium is air, n_0 is 1. It follows that the refractive index of the cladding (n_2) is key in the transmission of propagated light. If the cladding material were to be replaced by a coating that acted like a cladding but also changed its optical properties, like refractive index, due to the presence of certain chemicals in the environment; then we would have a very powerful sensor. The proprietary cladding utilized on the PetroSense® sensors is sensitive to petroleum hydrocarbons in the surrounding medium; this results in a hydrocarbon sensor. When hydrocarbons adsorb to the surface of the cladding of the fiber, the resultant change in the cladding refractive index (n_2) alters the amount of transmitted light. Very small changes in the refractive index can yield relatively large changes in transmitted light; these changes can be measured and calibrated to represent concentrations of species (e.g., TPH) present in the surrounding medium. This sensor can measure hydrocarbons in vapor as well as in water. As an example, the detection capabilities for the PetroSense® sensors for BTEX mixtures are 0.1 ppm dissolved in water, and 10 ppm in air. The lower detection limits for various hydrocarbons are shown in Table 1. As this sensor measures changes in the refractive index of the cladding it has a very large dynamic range. Measurements can be made from as low as a few ppm all the way up to saturation of hydrocarbons in air or water.

Third party testing has shown that the PetroSense® hydrocarbon probe has a greater than 95% correlation to a GC when measuring hydrocarbons under laboratory conditions.

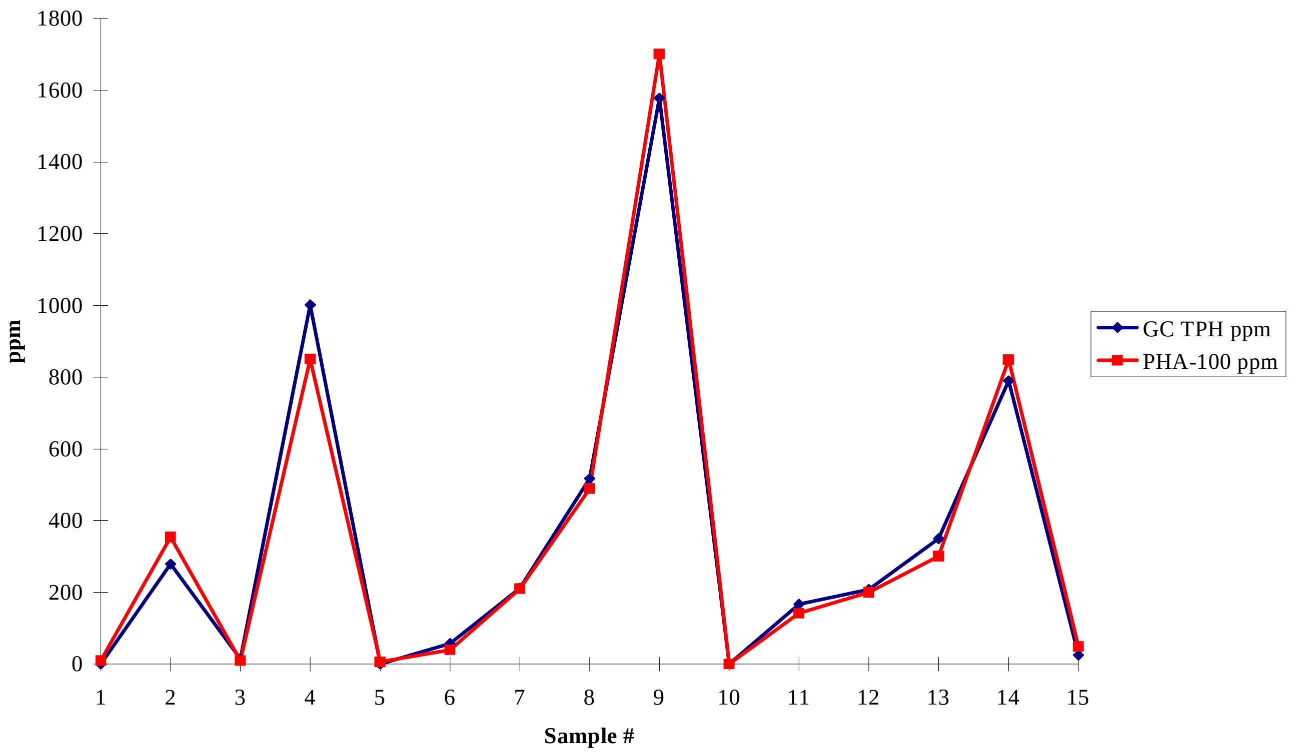
Compounds	**LDL for water (ppm)**	**LDL for Vapor (ppm)**
Xylenes (p, o, & m)	0.13	9.78
Benzene	0.38	54.45
Toluene	0.30	22.45
1,2,4-Trimethylbenzene	0.10	20.00
Ethyl Benzene	0.10	9.59
Trichloroethylene	5.00	65.00
Tetrachloroethylene	1.50	35.00
Unleaded Gasoline	0.40	3.00
Diesel	0.44	4.00
Kerosene	0.30	7.40
JP4	0.90	5.30
JP8	0.81	7.50
Bunker C/Num 6	0.35	3.00

Table 1 Lower detection limits for various hydrocarbons of the PetroSense® hydrocarbon sensors.

The coated fibers are built into probes (AHP-100, DHP-100 and DHP-485) that have the necessary electronics to convert the optical changes in the fiber to electronic signals that can be logged using a data logger. The probes are potted to allow the sensors to be used in water.

Figure 2 A PetroSense® hydrocarbon probe

These probes are used with various instruments such as the PetroSense CMS 4000 that has a data logger that can be connected to 4 probes. These probes can be left in situ for continuous monitoring of the environment for hydrocarbons. The probes are also used with a field portable instrument the PetroSense® PHA 100. These instruments show very good correlation to GC analysis of hydrocarbons (Graph 1).



Graph 1 Hydrocarbon vapor samples measured with a PetroSense® probe in-situ measurements and GC analysis

Summary

The use of fiber optic chemical sensor technology has allowed the creation of a unique sensor that is capable of measuring low levels of hydrocarbons in vapor and water. The sensors are unique because the measurements can be made in situ and in real time. This reduces errors from sampling as well as reducing analysis costs.

The PetroSense® instruments are being used in a number of applications where hydrocarbons need to be monitored. They are finding wide acceptance by the Oil industry as well as the environmental monitoring industry. The uniqueness of these sensors allows them to be used in process control and environmental monitoring. These sensors can be used either in vapor and water or in most environments where hydrocarbons are encountered.

References

[1] "Fiber Optic Chemical Sensor (FOCS®) Technology for the Detection of Hydrocarbons in Air and Dissolved in Water: PetroSense® Portable Hydrocarbon Analyzer (PHA 100) and the PetroSense® CMS 5000" D. P. Saini, R. Himka, S. Klainer, M. Arrasate, R. Leclerc, Field Screening Symposium, Las Vegas, Nevada, 22-24 February 1995.

[2] PetroSense® CMS 5000, A Fiber Optic Sensor Sensing System for the Continuous Monitoring of Hydrocarbons" D. P. Saini, R. Leclerc, S.M. Klainer, R.L. Himka, H. Arman, D.K. Dandge, O. W. Wolfbeis, B. Kovacs. 2nd European Conference on Optical Chemical Sensors and Biosensors, Firenze, Italy, April 19-21