PetroSense® Hydrocarbon Analyzers -- A New Tool for Static Soil Analysis

Stephen L. Coulter, Richard F. Leclerc, Devinder P. Saini
FCI Environmental Inc., Las Vegas, Nevada, U.S.A.
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PetroSense® Hydrocarbon Sensors and Their Applications

PetroSense® sensors represent a new technology for the detection of total petroleum hydrocarbons (TPH's). PetroSense® sensors are incorporated in both a portable, field screening instrument (the PHA-100) and a continuous monitoring system (the CMS-5000). These sensors utilize fiber optic systems and are designed for in-situ, real time measurements of TPH's and other related pollutants.

PetroSense® sensors operate in air (vapor), water and soil. PetroSense® sensors are non-specific detectors for TPH's, semivolatile 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 humidities, 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
- Water measurements in extracted 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 aboveground and underground storage tanks
- Leak detection for pipelines
- Storm water runoff monitoring
- Sample screening for laboratory analyses
- Site assessment
- Groundwater remediation

Whereas it has been mentioned that the sensors are non-specific, there is a relative response characteristic for the different compounds which 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® Technology

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.

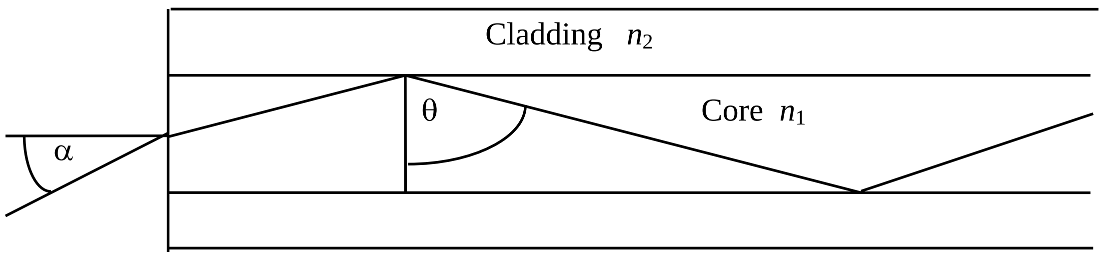

Figure 1. Schematic of an optical fiber: α is the acceptance angle; n_1 and n_2 are the refractive indices.

Light entering the end of a fiber optic is totally 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 of refraction, 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. The proprietary cladding utilized on the PetroSense® sensors is sensitive to materials in the surrounding medium, which results in an environmental chemical sensor. As materials such as TPH's associate with 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 calibrated to represent concentrations of species (e.g., TPH's) present in the surrounding medium. As an example, the detection capabilities for the PetroSense® sensors for BTEX mixtures is 0.1 ppm dissolved in water, and 10 ppm in air.

Static, Real Time Analysis of Soil Samples

The PetroSense® Portable Hydrocarbon Analyzer (PHA-100) is a valuable tool for the static, real time analysis of soil samples. There are a number of potential problems and sources of artifact in soil analysis. To be effective in the analysis of soil samples a standard methodology is needed along with instrumentation, which can provide reproducible results. Inherent in all soil analysis methods is the difficulty in establishing consistent headspace concentrations of the contaminants. A second problem is the weakness of standard methods in the determination of semivolatile TPH's (e.g., diesel, fuel oils) due to their lower vapor pressure in air.

The PHA-100 has recently been accepted as a method for the determination of "Excessively Contaminated Soil" for TPH's as set forth in Rule 62-770.200(2), Florida Administrative Code. The previous standard has been the use of a Flame Ionization Detector (FID). The performance of the PHA-100 was compared to that of a Thermo Environmental Instruments Inc. FID, model # 680 HVM. Both instruments were calibrated according to manufacturer's instructions. Measurements were made in a Tedlar® bag, with 7 liters of air, at room temperature. The individual performances against several hydrocarbons were compared. Figure 2 represents the direct relative performance of the PHA-100 against the FID for unleaded gasoline, diesel fuel and jet fuels (JP4 and JP8). As

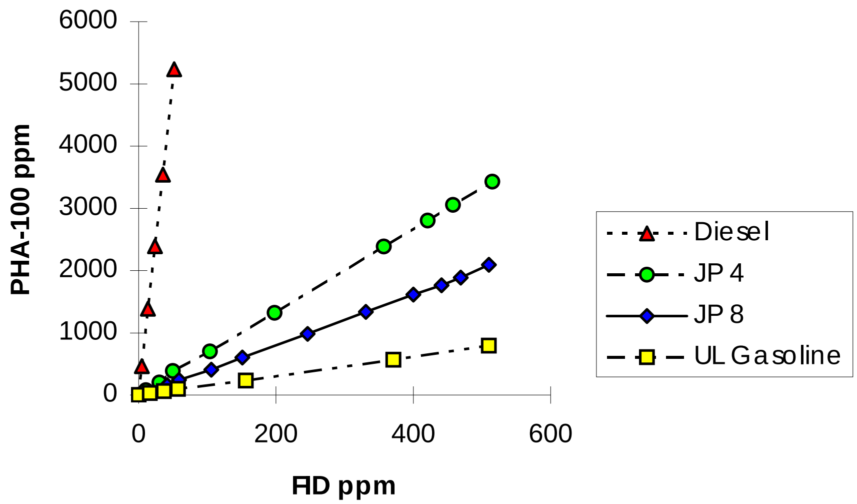

Figure 2. Comparative response of the PetroSense® PHA-100 to an FID.

can be seen, the less volatile, heavier hydrocarbon blends have a much higher RRF as compared to the FID. This allows for a much higher sensitivity of the PHA-100 to the contaminants, which are particularly troublesome to many methodologies due to their low volatility. When the PHA-100 readings are corrected with the appropriate RRF's, the correlation for all of the tested compounds with gas chromatograph analyses was better than 99.9%.

Along with an improvement in the sensitivity of the instrumentation, a reproducible, standard methodology is necessary for effective soil analyses. The effect of humidity, ionic content and pH of the soil medium were evaluated. The TPH's absorb to soils with a certain affinity related to the composition of the soil. A soil jar designed to accept the PHA-100 probe was always filled to one half the total volume with soil to provide a reproducible response in the tests. Saturating the soil with water resulted in more uniform measurements with shorter equilibration times. The water helps to break up the soil and disperse the absorbed hydrocarbons more effectively. The water also helps to achieve a uniform humidity, which affects the amount of volatilized hydrocarbons, and aids in the stabilization of temperature within the jar due to better thermal conductivity. The addition of salt (approximately 3 weight percent with respect to the water) provides additional assistance in driving the hydrocarbons into the vapor phase. While the water helps to dissociate the hydrocarbons from the soil, the ionic concentration in the water decreases the solubility of the hydrocarbons in water resulting in a higher partitioning of the hydrocarbons from the water into the vapor. The other approach evaluated was the use of pH to affect hydrocarbon vaporization. By driving the pH of the water to less than 3, the partitioning effect was also seen. The effect of the pH was as effective, or greater than that for the salt.

The use of the PHA-100 for soil analysis is a static method. No pumping is needed, which eliminates another source of artifact in soil headspace analysis. The PHA-100 analysis is non-destructive, which, along with being a passive, static measurement, allows for more uniform and stable readings.

To maximize the efficacy of soil analysis the recommendation would be to utilize a reproducible test method. The use of salt water and/or acidic water maximizes the dissociation of the hydrocarbons from the soil and the partitioning from the water into the vapor.