Measurement of Hydrocarbons in Produced Water Using Fiber Optic Sensor Technology

(An Alternative to Freon Extraction and IR Analysis Methods)

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Abstract

Due to the non-availability of Freon, there is need for an alternative method to measure the concentration of hydrocarbons in the effluent from oil water separators in use in the oil industry today. Current methods use solvent extraction and IR analysis of water samples. In this paper we present an alternative method, which does not use any solvents and can provide in-situ analysis of the hydrocarbon concentration in water. This method is based on FCI Environmental Inc.'s fiber optic chemical sensor (FOCS®) technology. It provides accurate and reliable data to improve overall water processing on platforms. The instruments have been extensively tested by a number of companies on their platforms in the Gulf of Mexico and the North Sea. There are now over 120 instruments being used in the Gulf as an alternative to solvent extraction.

Introduction

In order stop the depletion of the ozone layer in the upper atmosphere; countries adhering to the Montreal Protocol have stopped the use of volatile chlorofluorohydrocarbons. This has caused a problem for the monitoring of oil-in-water using Freon extraction and analysis by Infrared. The US EPA and the European regulatory authorities require the monitoring of effluent water for hydrocarbons. Most of the methods that are approved for determining the hydrocarbon concentration in water use Freon or other solvents. These solvents extract the hydrocarbons from the water sample so that the concentration can be determined. The solvent along with, the sample are then analyzed using the C-H absorption band at 3.4 microns to determine the hydrocarbon concentration.

Due to the Montreal Protocol, the cost of Freon has increased considerably due to the lack of availability. This has hindered the organizations striving to adhere to the EPA regulations regarding the presence of oil in effluent waters. Clearly, there is a need for alternative methods of determining the oil-in-water concentrations where solvents are not used. In this paper we present an alternative method of determining the concentration of oil-in-water using the FCI Environmental Inc. (A DecisionLink Company), hydrocarbon probes (DHP-100 and DHP-485).

The presence of petroleum hydrocarbons in water is detected using a patented Fiber Optic Chemical Sensor (FOCS®). The FOCS® probe takes advantage of the interaction between the light traveling through a fiber (with a proprietary coating) and a water solution containing petroleum hydrocarbons.

PetroSense® Hydrocarbon Sensors

PetroSense® sensors [1,2] 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-100WL) and a semi-continuous monitoring system (OilSense®-4000) for the monitoring of effluent 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.

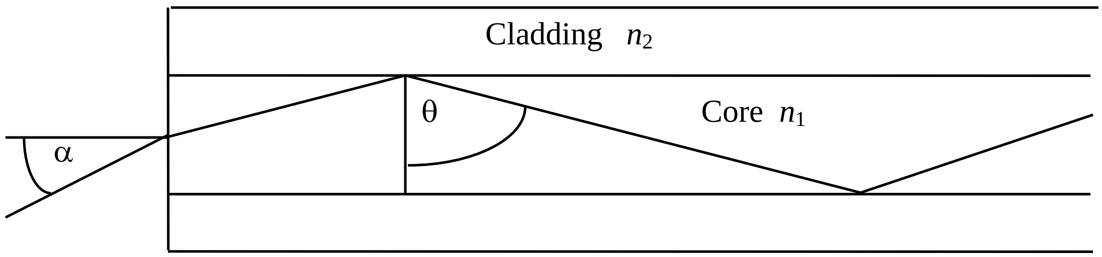

Figure 1. Schematic of an optical fiber: α is the acceptance angle; n_1 and n_2 are the refractive indices.

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. 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.

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 then used in conjunction with the PetroSense® PHA-100WL.

The PetroSense® PHA-100WL

Figure 3 A PetroSense® PHA-100WL

The PetroSense® PHA-100WL is a hand-held meter that is used to measure the oil-in-water content of grab samples. It is used in a similar manner to the solvent extraction method except that no solvents are used. A water sample is taken and split into two equal parts. One part is put trough a carbon filter to remove the hydrocarbons. The filtered water is used as the background "zero" water. The probe is placed in this water and zeroed. After zeroing the probe is then placed in the second half of the sample water and a reading is taken. The instrument provides a frequency output that is related to actual hydrocarbon concentration using a simple chart. The PHA-100WL is used at EPA sample points, for water system trouble shooting and upstream monitoring. Its use reduces operator variables in sampling and allows for better additive management.

Field Tests

The PHA-100WL has been extensively tested in the field. The tests consisted of direct comparisons with existing field methods. The typical results are shown on Figure 4. These results show excellent correlation with the current solvent extraction sampling methods being commonly used in the field. Figure 5 is a scatter plot, of the PHA vs. the IR method over a hydrocarbon concentration range of 0 to 400 ppm. This also shows a strong correlation between the two methods. The data shows that the PHA can measure hydrocarbons in water over very large range and still maintain good correlation with IR methods. The PHA requires less time than the solvent extraction method to determine the oil in water concentrations. On average it only takes 15 minutes or less for a measurement whereas the solvent extraction method can take up to an hour.

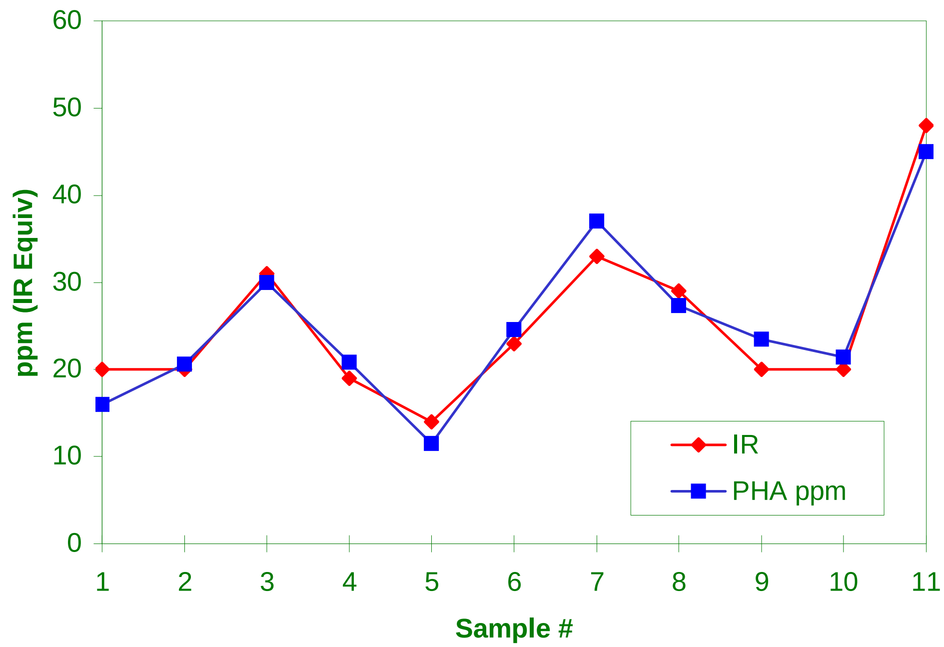

Figure 4 PHA-100WL Comparison with IR - Offshore Platform Field Test

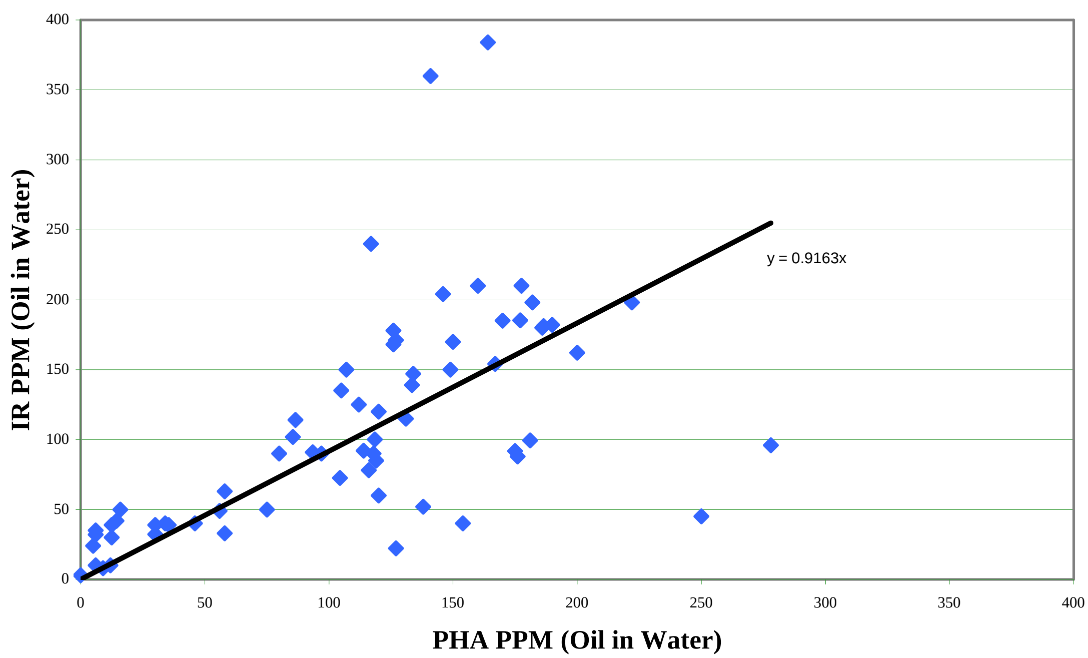

Figure 5 Comparison PHA vs. Solvent Extraction IR
Range 0 to 400 ppm

Discussion and Conclusions

The results presented in this paper clearly indicate that fiber optic based technology has provided a solution to the measurement of oil-in-water. Furthermore this technology does not use any solvents and therefore provides a long-term solution.

The PHA-100WL have been extensively field-tested and are currently being used on oil platforms in the Gulf of Mexico. The instruments are used to measure hydrocarbon concentrations in produced water before it is discharged to the sea. The hydrocarbon levels measured by the the PHA-100WL in this application range from 3-400 ppm. The hydrocarbon probe used is linear to approximately 100 ppm and can detect concentrations greater than 1300 ppm.

The ease of use and the zero solvent usage in operation of these instruments make them highly suitable devices for the monitoring of effluent water. These instruments can easily replace the existing Freon extraction method for determining the hydrocarbon concentration in water. There are over 120 of these instruments being used in the Gulf of Mexico today. The widespread use of these instruments is a clear indication of the acceptance of this technology in the field.

The PetroSense® technology provides systems that can measure concentrations of hydrocarbons in-situ without the use of solvents. This ability allows the users to obtain better information, faster concerning the operation of the platform. This leads to greater efficiency and cost savings. The PHA has proven itself to be reliable and user friendly and above all provides accurate oil in water measurements without the use of solvents.

References

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[2] "Comparison of Measurements with PetroSense® Portable Hydrocarbon Analyzer (PHA 100) and Laboratory Analysis of Bailed Samples (EPA Method 8015M) When Used in Monitoring Sparging Process" D. P. Saini, T. Wing, D.K. Dandge, R. Leclerc, presented at Field Screening Symposium, Las Vegas, Nevada, 22-24 February 1995.