

New Sampling Procedure for Fluorescence and Other Instruments

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This title was originally to be presented by Jeff Keathley of Oilfield Analytics. Jeff was a key player in the development of this procedure. In memorium to Jeff, Arjay Engineering presents this alternate paper to highlight the procedure he worked on.

Introduction

Low concentration monitoring of oil in produced water continues to be a vital measurement parameter in the offshore production of crude. The driving forces to do so may have evolved over time but the underlying need remains the same.

One of the more obvious concerns to oil in overboard water is lost product which can directly affect profitability, however, in the overall scheme of a typical platform, lost product in produced water can be negligible when factored against the rewards of high volume output. The true economic drivers may be less obvious.

Oil in water monitoring provides a direct indication of separation efficiency. Using a monitor as a Preventative Maintenance Tool provides operators with the foresight to ward off impending mechanical issues of separators that may eventually lead to costly downtime. Monitoring the separator output for trace hydrocarbons also enables an operator to tune the process to maximize production efficiency (process optimization). This is often done through the manual or controlled release of chemical additives at various stages in the production process or through variable process tuning such as flow, temperature, and pressure.

Another key need for monitoring hydrocarbons in produced water is the issue of disposal. Water released to the environment is typically regulated under tight authority for pollutants and requires routine monitoring. In the USA, the Clean Water Act directs the National Pollutant Discharge Elimination System (NPDES) permit program to control and monitor discharges, which includes hydrocarbons in water.

It is both the economic and the environmental factors that have initiated the development of an alternative sampling procedure that will provide fast reliable results with minimal handling.

Historical Premise

There are several technologies readily available to monitor for ppm concentrations of hydrocarbons in water.

Most of these technologies are optical and include:

- Light scatter / turbidity
- Colorimetry
- Infrared
- UV Absorption
- Fluorescence
- Imaging
- Gas Chromatograph
- Ultrasonic

Historically, instruments for offshore use were limited to benchtop designs. On-line instruments for offshore use were introduced 15 or 20 years ago and within the past 10 years there has been a dramatic increase in the variety of these products for offshore monitoring. Industry's realization of the economic importance of monitoring in conjunction with tighter regulatory controls has driven this.

For land based wastewater measurements, GC-FID gas chromatography is used by many accredited labs for the analysis of petroleum hydrocarbons in water. The flame ionization approach, associated maintenance and sample preparation methods are not conducive to offshore use. This is also not the approved analytical method for offshore produced water.

In the Gulf of Mexico and various parts of the world, a long established technique of sample monitoring for offshore oil in water was directed under EPA Method 413.1 This was a Freon extraction methodology to remove certain hydrocarbons from the water. The procedure then required a drying and weighing of the residue. This detailed and intricate measurement method is also not conducive to offshore use and samples would routinely be sent to shore for analysis.

An alternative to the gravimetric approach was infrared. This method employed an infrared instrument to measure energy absorption based on the number of hydrocarbon bonds in a hydrocarbon sample and correlate this to an oil in water concentration. The Foxboro Miran dominated offshore platform use for many years. The Foxboro products are not available anymore and the Wilks IR instrument has become a formidable choice as well as instruments from companies like Horiba.

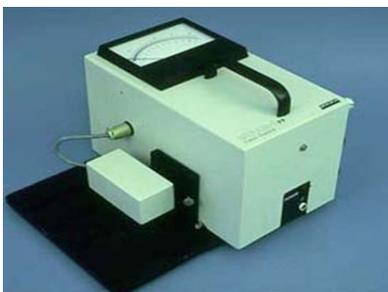


Photo 1. Now obsolete, the Foxboro Miran IR monitor was used offshore.



Photo 2. The Wilks IR is a typical replacement to the Miran.

Infrared technologies were based on a Freon solvent extraction of the hydrocarbon from water prior to analysis. Through participating country treaties under The Montreal Protocol which was initiated in 1987 and lead up to the year 2000, there are now extreme worldwide limitations on the production of Freon. As such, the EPA has abandoned Method 413.1 in favor of Method 1664A. Method 1664A uses a hexane solvent extraction procedure and through a process of evaporation and drying, weighs the residual oil sample to determine a mg/l result. This is referred to as a gravimetric approach.

Like the GC methods, the procedures for sample preparation under Method 1664 are very detailed and susceptible to technician and laboratory inconsistencies. These include sample preparation measuring, lag time for sample testing, cross-contamination, and scale instrument errors.

The gravimetric approach, like the gas chromatograph approach, has not been a viable method for offshore analysis. As such, there presently is not an approved analytical method routinely used offshore for the determination of oil in water.

Typical Approved Analytical Methods Used to Define and Measure Oil in Water Concentrations

GC - FID	Infrared (IR)	Gravimetric
ISO-9377-2	EPA 413.2	EPA 1664A
Pentane extraction	Freon Extraction*	Hexane Extraction
OSPAR Europe (North Sea)	Various others	EPA USA

*ASTM Test Method D 7066-04 approved S-316 as an alternative solvent for the IR method

This short evolution of analytical methodologies and associated instrumentation was a result of the abolishment of Freon due to its ozone depleting issues. During this time, fluorescence instruments were gaining notoriety for offshore use, both in their on-line and benchtop designs. Fluorescence has been recognized as a valuable tool for analytical sciences for many years and the evolving need for alternative methods offshore drove the development of robust fluorescence instruments to be used in the petroleum industry.



Photo 3. Fluorescence instruments, like this Coleman unit from the 1940s, have been around a long time.



Photo 4. Today, fluorescence units like this Arjay FluoroCheck offer many interface and unique user features.

Fluorescence instruments target the aromatic component of the produced water sample. They do not require a solvent extraction to prepare the sample. A straight produced water sample can be measured directly in the instrument

The various solvent extraction procedures employed by analytical methods were not solely to accommodate IR instruments. They also provided a method to qualify the oils to be reported to the regulating authorities. Basically, what is extracted using a defined solvent method is what is to be reported.

To make benchtop fluorescence results more representative of analytical methods, a solvent extraction is typically performed on a sample prior to transference to the instrument. Method 1664 uses hexane and since hexane solvents do not fluoresce, the extracted samples can be put directly into an instrument without fear of interference. Evaporation or drying procedures are not required.

Since the duty of an on-line fluorescent instrument is to respond instantaneously and perform continuously 24 hours/day, a solvent extraction procedure is not performed for on-line instruments. Some of the instabilities of the raw water readings are accommodated through filtering and averaging software.



Photos 5,6, & 7. On-line fluorescence instruments provide continuous monitoring without the use of solvents, consumables, or sample preparation. Shown from left are the Arjay HydroSense, the Turner 4100 and the Advanced Sensors OIW.

One of main issues of qualifying samples to an approved method through solvent extraction is the use of the solvent itself. It can be expensive to procure; it is a hazardous material that requires both specialized transportation and handling care; and it must be disposed of properly. Non-hazardous solvent alternatives have recently been introduced that provide a safer means to extract and measure samples.



Photo 8. Solvents, such as hexane, are used to extract hydrocarbons from water and help to define the oil to be measured.

Procedures that require multiple steps to sample preparation and analysis can introduce inconsistencies and errors to the readings if not followed properly.

A quick re-cap indicates the premise to which the alternative grab sample approach was developed.

- Offshore sample measurements of oil-in-water require a multi-step sample preparation.
- There is not an accredited and reportable offshore method.
- Solvents for extraction are expensive and hazardous
- Routine and frequent samples for oil in water concentration are of high value to operators

Alternative Sample Procedure

The sample procedure investigated by Oilfield Analytics was to marry the non-solvent on-line approach with the low maintenance and reliability of a benchtop instrument. Named the CT-1000, the sample delivery mechanics was designed to deliver a large water sample through a benchtop instrument in a consistent and repeatable manner.

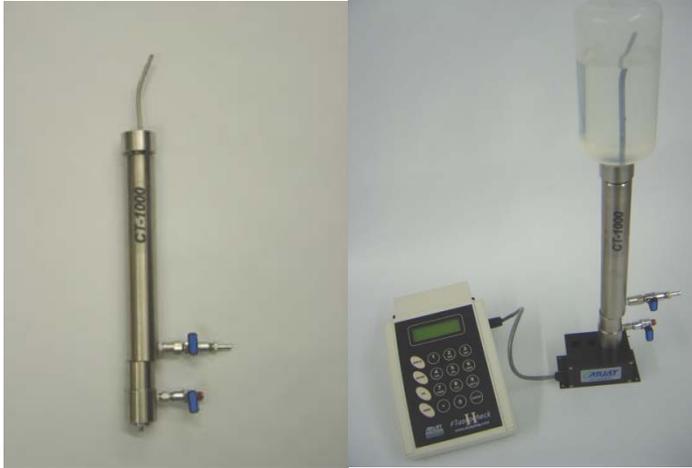


Photo 9. A sample delivery system free from measuring, extractions and chemicals is the premise the CT-1000.

Loosely based on the law of large numbers probability theory, the simplified sample delivery assumes that an average of a large set of oil in water readings will more closely resemble that of the expected result than a single sample reading. The more the readings, the closer the expectation.

A manual grab sample is taken in routine fashion from the process. A one liter container can be drawn in a composite sample mode using multiple draws from a process or it can be a discrete sample mode drawn using a rapid or slow stream. These draw options can provide the operator with greater flexibility in his targeted data and will be more representative of the true result.



Photo 10 & 11. The CT-1000 can accommodate various bottle sizes.

The CT-1000 is designed to readily accept multiple sample bottle sizes and can make use of the standard offshore glass bottle or larger Teflon lined bottles. The drill press format allows for a fast maneuver into the fluorescence instrument and includes an air vent tube to allow a continuous free flow of the sample through the instrument.

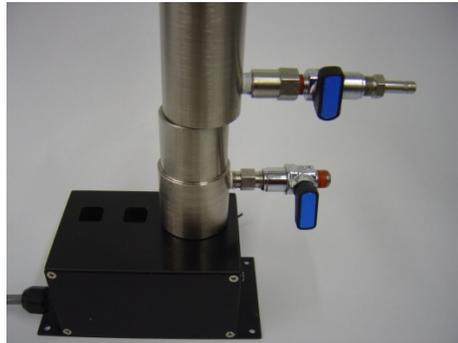


Photo 12. An air valve and a sample valve provide for a stable and continuous flow through the instrument.

The unit is designed to accommodate round or square disposable cuvettes which eliminates the need for clean up due to cross contamination of samples. The CT-1000 is designed to work with existing field instruments or any instrument that uses industry standard cuvettes.



Photo 13. The CT-1000 can accommodate various cuvet sizes and styles.

Arjay Engineering, a manufacturer of fluorescence instruments, has supported the development of this project through the customized design of a special cuvet block design and CT-1000 software.



Photo 14. The cuvet block is remote from the instrument for ease of use.

The cuvet block has been made remote from the main electronics for ease of use and operator interface with the electronics display and interface. The remote cuvet block is detachable from the main unit.

The instrument package can accommodate multiple LED wavelengths and are typically offered in a 250 nm and 360 nm excitation versions.

Keypad entry of the LED intensity extends the range of the instrument from low concentration, low intensity oils through to high concentrations. To increase the accuracy over wide ranges, a multi-point calibration curve may be entered with up to 5 concentrations.

The FluoroCheck can accommodate up to 10 different calibration curves. A platform, for example, can have a programmed calibration curve for an straight water sample and a second calibration for solvent extracted samples.

The RS-232 interface allows an operator to interface to a printer or computer to access all the reading data.

A sample run time is determined and held in the memory. Upon presentation of the sample to the CT-1000, the flow valve is opened and the FluoroCheck is initiated. A 10 second flow is ignored to allow a fresh sample to flow through the cuvet.

Sample readings are logged at a rate of 10 samples per second as the water sample passes through the cuvet. A typical one liter sample streams through in about 6 minutes and will produce 3,600 logged readings. The FluoroCheck automatically ends the logging events based on the predetermined run-time or can be manually interrupted.



Photos 15, 16 & 17.. The display allows for easy set-up and shows active readings as the sample streams through

Upon completion, the display will read the highest, lowest and averaged reading. Should an operator determine that a solvent extraction should be performed on a sample, the multi-calibration library feature will provide a quick switchover to allow a manual extracted sample to be inserted into the well.

Arjay has performed tests of the CT-1000 with the following encouraging results. These tests are based on prepared sample in a controlled lab. Actual process conditions would expect to result in a greater variance from high to low values, which stress the importance of this streaming average approach even more.

CT-1000 Prototype Test 1

Calibration Data

BLOCK 1				BLOCK 2			
Diesel (LED=10mA)	0 ppm	120mV	Reference B	Diesel (LED=10mA)	0 ppm	150mV	Reference B
	35 ppm	1195mV			35 ppm	1656mV	
Crude (LED=1mA)	0 ppm	10mV	Reference A	Crude (LED=1mA)	0 ppm	26mV	Reference A
	20 ppm	783mV			20 ppm	872mV	
Cal. 4 (LED=20mA)	0 ppm	150mV	aged 100 ppm Crude oil	Cal. 4 (LED=20mA)	0 ppm	150mV	aged 100 ppm Crude oil
	50 ppm	520mV			50 ppm	580mV	

Test Result

BLOCK 1					BLOCK 2				
Model:	CT-1000/FC II				Model:	CT-1000/FC II			
Serial No.:	0914134				Serial No.:	0914132			
Part No.:	A00721, A00722				Part No.:	A00721, A00722			
Description:	Oil in water Monitor				Description:	Oil in water Monitor			
	Clean Water (Diesel)	Diesel	Clean Water (Crude)	Crude		Clean Water (Diesel)	Diesel	Clean Water (Crude)	Crude
Average	1.0	8.2	0.1	46.2	Average	0.8	7.4	0.1	49.0
Hi	1.1	8.6	0.1	48.0	Hi	1.0	7.7	0.2	50.9
Lo	0.8	8.0	0.1	44.9	Lo	0.7	5.5	0.1	47.3

Note:

1) Diesel sample Test result based on Reference B calibration Data.

Chart 1. Tests using prepared crude oil in water samples show a variance of over 3 ppm (7% of expected reading) can occur in a controlled laboratory test. Field variances could be even more dramatic.

The CT-1000 is designed to compliment existing offshore monitoring equipment and accredited shore analysis, not replace it. Since the sample delivery system and accompanying fluorescent instrument are not a regulated analytical method, the user is free to follow procedures and calibrations that are most suited to his own need. Results are for trending observations of process conditions and are not required to be reported.

The CT-1000 will allow operators to monitor samples from various sample points and verify on-line monitors and process systems with a reasonable degree of accuracy and reliability in a fast and easy method. This in turn will support operator comfort in using laboratory instrumentation and improve the availability and confidence of produced oil in water data.

A patent has been applied for the CT-1000 and field tests at production facilities have been determined.