"UV Fluorescence for Monitoring Oil and Grease in Produced Water – Real Data from the Field"

By

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"Monitoring Produced Water using UV Fluorescence (UVF) technology provides high correlation to oil and grease as defined by official laboratory methods. On-line units and bench top units are available providing excellent reliability, high accuracy and repeatability ease of use and low maintenance with high correlation to official lab data. Bench model UVF units produce reliable results in 4 minutes or less!!"

Do you believe all that?

Issues covered in this paper:

"UV Fluorescence can't work because it only measures the aromatics not the total oil".

"UV Fluorescence can only monitor totally dissolved oil and not droplets".

Recommendations to Potential Customers of Oil in Water Monitors:

Analyze the technology and determine how it works.

Analyze the instrument system and the sample system.

Demand to see the hard data from the vendor!

First, some absolutes for acceptance of any instrument by Produced Water Customers:

1. **The instrument must provide meaningful data.**
   Calibrated Instrument (through blank and standard addition)
   Correlated Instrument (correlated to acceptable laboratory methods)

2. **The instrument must be VERIFIABLE in the field**
   Recalibrate with standards or analyzed samples
   Verifiable check standard

3. **The instrument must be low maintenance**
   Easy Cleaning
   Minimal maintenance issues

1. The Instrument Must Provide Meaningful Data

1.1 Calibrated On-Line Instrument

A properly calibrated instrument using a user acceptable method and user acceptable analyte provides meaning full data.

Calibration of any on-line units regardless of technology:

Classic calibration of any instrument means having 2 or more points of different concentration. One is a blank (zero concentration) defined as the matrix fluid void of the target analyte or analytes. The other point(s) (known standard) is a known concentration of the analyte in the blank matrix. In the measurement of oil and grease in produced water, the blank is the produced water without the target oils and the known standard must be made from adding the oil back into the blank. In most cases of produced water not only is it difficult or nearly impossible to create a matrix water blank but it is equally difficult to add back crude oil into the water blank. If it were possible to create a blank and standard, a very high skill level of trained technician/ Chemist would be necessary to perform the procedure. Technically, adding crude oil to a blank would only at best approximate actual laboratory results because the oil and grease in produced water measured by the laboratory method is not only crude oil but a complex mixture of organic compounds and oil.

(An alternate calibration of 2 random concentrations is available on the Turner Designs on-line instrument. However, the 2 points must rely on accurate lab analysis of the samples. If this method is used, we suggest 3 samples at each concentration with the results averaged and a large span between the 2 concentrations.)

The factory recommended calibration of on-line instruments for produced water oil and grease measurement is through correlation to an acceptable lab oil and grease method or acceptable surrogate field bench methods. The more samples analyzed the more confidence in the resultant correlation.

1.2 Correlated On-line Instrument

Correlation – the mathematical relationship between 2 sets of data. The relationship is defined by the least squares also known as the R^2 value where R^2 = 1 represents a straight line. The R^2 defines the 2 data set's proximity to a straight line and defines a "best fit" line between the data points. For oil and grease measurements consider anything above R^2=.8 to be "good" and anything above R^2=.9 to be excellent. The more data points and the larger the spread between concentrations, the more confidence in the correlation.

For correlation, grab samples are analyzed against readings from the instrument and a correlation graph is developed similar to the data shown below.

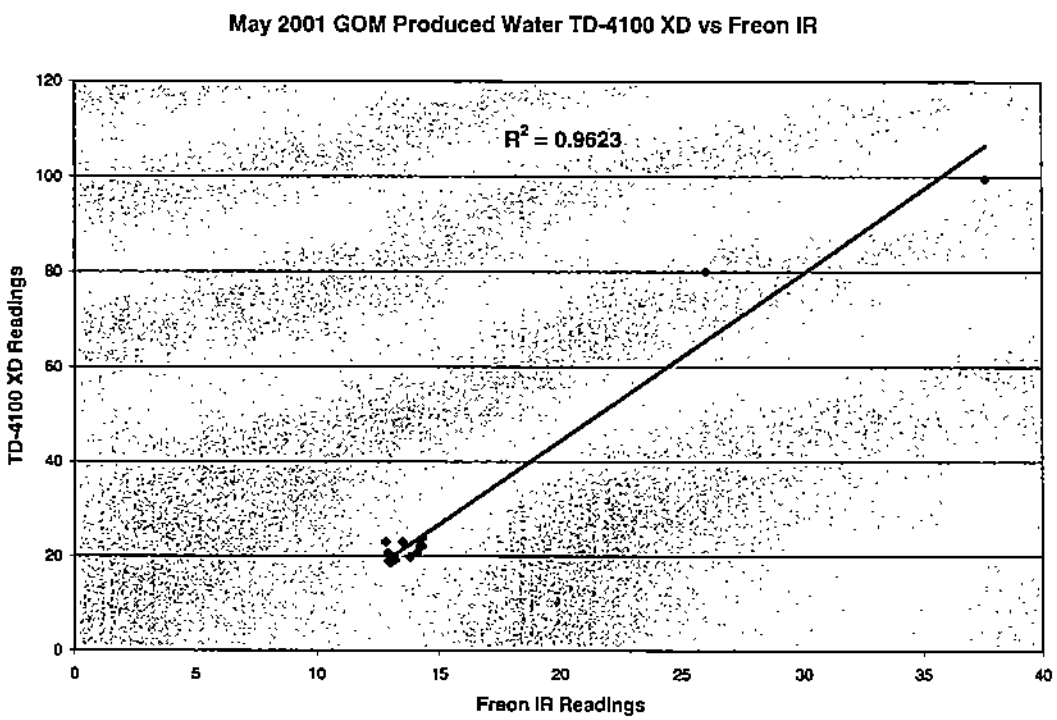


Figure 1

The grab sample analysis can be by the official laboratory oil and grease method used in the specific country or an acceptable and reliable field method known to produce similar results. We do not recommend the "colorimetric" method be used as a field method due to inconsistencies between locations and operators and typically poor correlation to the official oil and grease method.

Special note regarding collection of grab samples:

Because the correlation of the on-line unit requires a grab sample analysis, we recommend 3 identical samples be analyzed for each sample point with the results averaged for each point. This will reduce the potential error inherent in the lab analysis method.

Note regarding use of non-matrix fluids for calibration:

Calibration of on-line units by "blanking" and standard addition of oil or dilution of produced water with fresh or other non-produced water sources is not acceptable. This method produces false calibration and an incorrect calibration slope. Theoretically, a blank could be manufactured by taking a volume of produced water and stripping all the oil and grease by washing the water with designated solvent, but then the problem is to add the oil back into the blank water.

1.3 Calibrated Bench Model Instrument

There are 2 widely used methods for calibration of bench model fluorometers. 1) Solvent blank with pure crude oil added to the solvent and, 2) Use of the official oil and grease method to assign concentration to parallel samples.

Blanking with bench-top UVF units is not an issue because solvent extraction methods dictate blanking with the solvent. Adding crude oil to the solvent to create a standard is widely used in cases where an acceptable alternate lab method is not available. However, measurement of the crude into the solvent blank can be tricky and requires skill and the correct lab equipment. Most operators accept crude oil in blank calibrations as only a surrogate "ballpark". When using the crude oil in solvent blank method of calibration, we suggest water samples be analyzed by an official method as soon as possible to validate the calibration or to determine an offset of the reading.

It is recommended that for best results, calibration of the bench-top unit be performed using the official lab method. Parallel samples can each be analyzed by the bench model and the official method with concentrations assigned based on the official results. We recommend 3 samples for each concentration point with the results averaged.

2. **The instrument must be VERIFIABLE in the field**
   All instruments must be able to be either recalibrarted easily or a method must be available to verify the performance of the instrument.

On-Line Units: If recalibration is impossible due to matrix issues (produced water) then a suitable alternative method must be employed. An adjustable solid UVF calibration standard is available. After initial calibration of the instrument the solid standard is inserted into the instrument through the viewport with the sample water turned off. The instrument reading using the solid standard is adjusted to match the desired concentration. The resultant number is recorded on the solid standard. Later, whenever the instrument is questioned, the water is turned off and the solid standard inserted. The instrument does not need adjustment if the reading is within 10% of the original reading (or a threshold set by the customer). We also recommend that the on-line instrument be read whenever a monthly grab sample is taken.

Bench Model: Once initial calibration is set, the adjustable solid standard is set within the readable range. Since the instrument is blanked with the solvent, the calibration can be reset to the solid standard for future field calibration. Once in the field, the operator checks the calibration with the solid standard. If out of the

desired range, the operator performs the calibration sequence with the blank solvent and the solid standard.

Alternately, the bench model with the extraction method can be recalibrated with crude oil added to the blank if this method is acceptable to the customer.

As with all instruments, we recommend parallel grab sample analysis be performed whenever an official sample is taken.

3. The instrument must be low maintenance

On-line UVF Instrument: Instruments are available offering UV Fluorescence technology with true non-contact of the water (see Technology Discussion Below). These instruments offer the highest reliability and lowest maintenance in the offshore industry as long as the sample lines are maintained. In applications with reliable flow and clean sample lines, 3 – 6 months can be expected between maintenance events. However, the sample lines must be kept clear for minimal maintenance.

Bench Model UVF Instrument: If the bench model UVF instrument is located in a non-corrosive atmosphere the user can expect many years of trouble free service. Salt air and corrosive atmosphere will increase the likelihood of more frequent maintenance.

"UV Fluorescence can't work because it only measures the aromatics not the total oil". – Quoted by Infrared Absorption instrument salesmen worldwide.

While it is true that UVF only measures aromatics in oil applications, in most cases it does not matter because the signal from the aromatics remains fairly constant relative to the total oil. During calibration of the UVF instrument the signal from the aromatic content is assigned a value based on analysis. The proof is in the ***data (see below).***

Note that there are some cases where oil and grease do not fluoresce such as animal or vegetable oils – this is not the market for the UVF instrument. In other applications there may be many different kinds of oils and greases present in varying concentrations that would confuse the instrument. This is also not the market for UVF.

Although the UVF instrument only measures the aromatic fraction, data below is conclusive evidence that the calibrated UVF instrument measures total oil and grease.

The correlation to total oil and grease as measured by standard addition methods: (for complete report visit www.turnerdesigns.com/t2/oiwm/oiwm.html).

Oil in this test was standard for the IMO Bilge test - light distillate fuel oil.

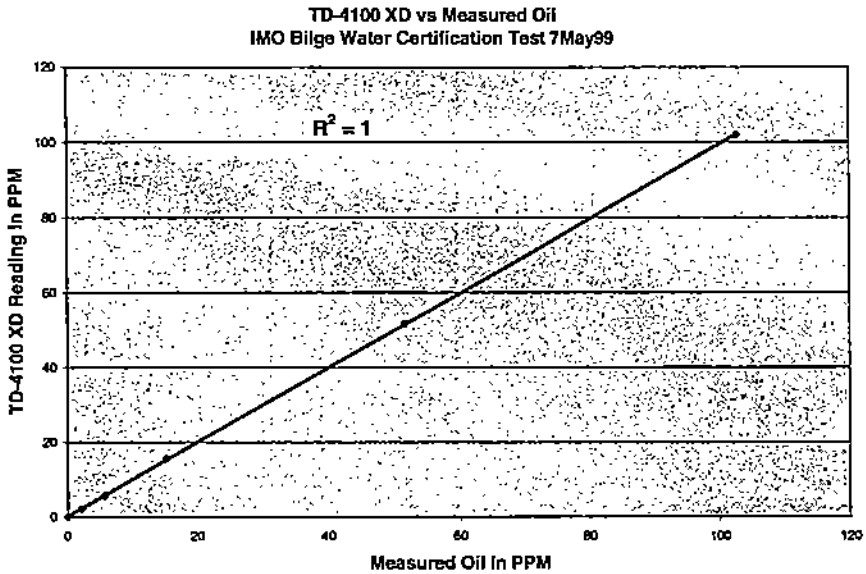
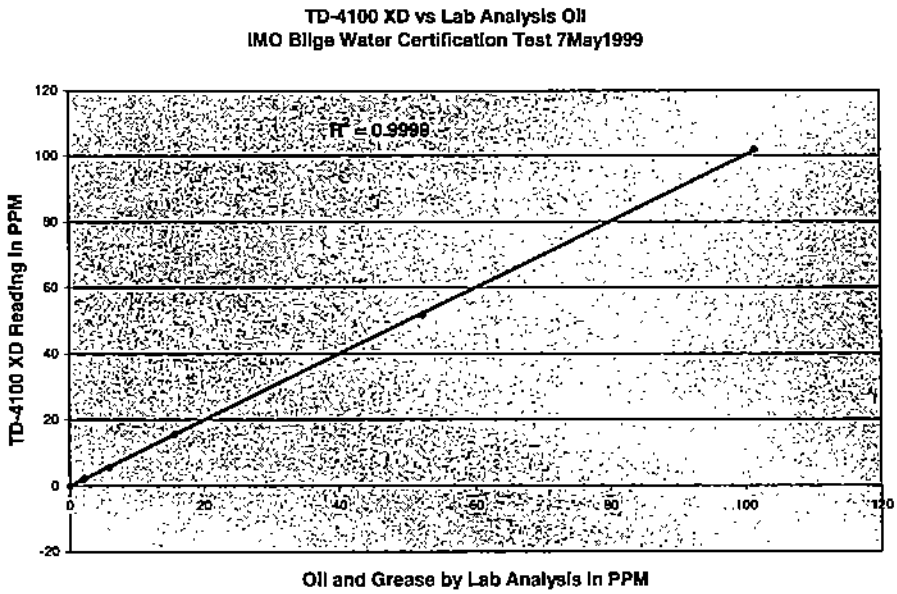


Figure 2



Same Test Data versus Laboratory Analysis

Figure 3

UVF Monitors Oil and Grease in Produced Water

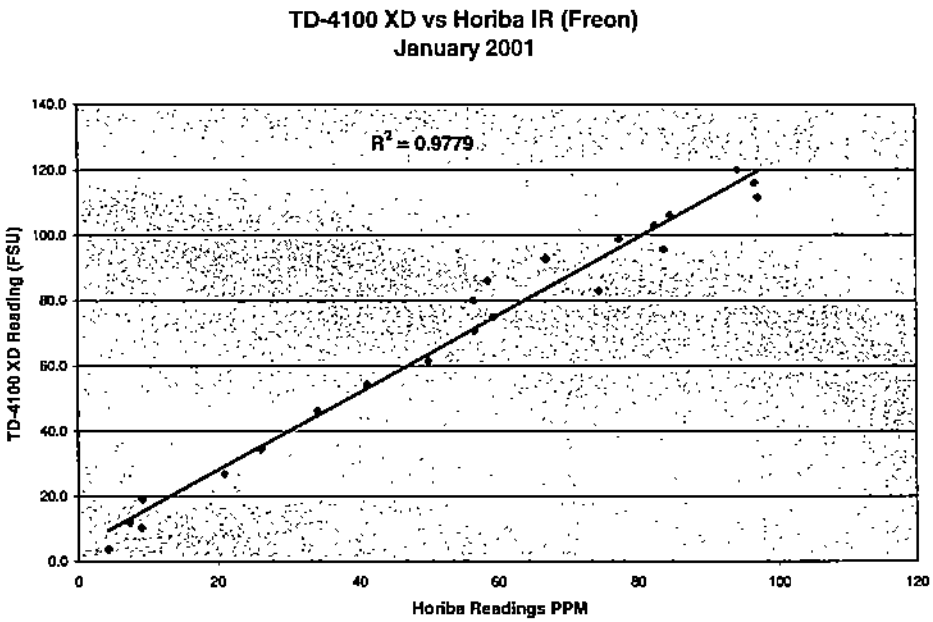


Figure 4

Correlation TD-4100 XD and Horiba IR Horiba solvent.

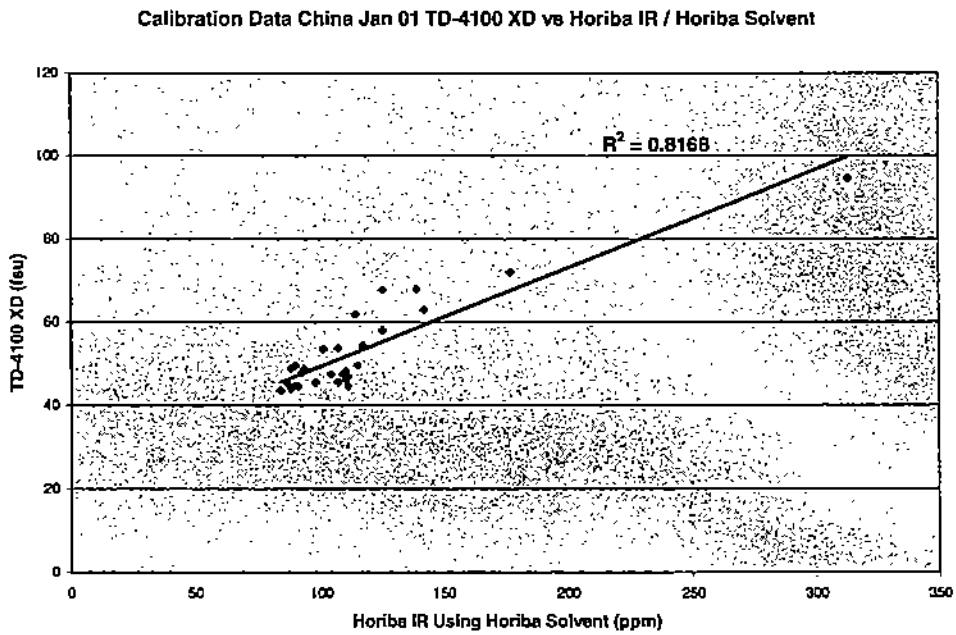


Figure 5

Example of on-site calibration of the TD-4100 XD and the TD-360. The TD-360 was calibrated using crude oil in Hexane as a standard.

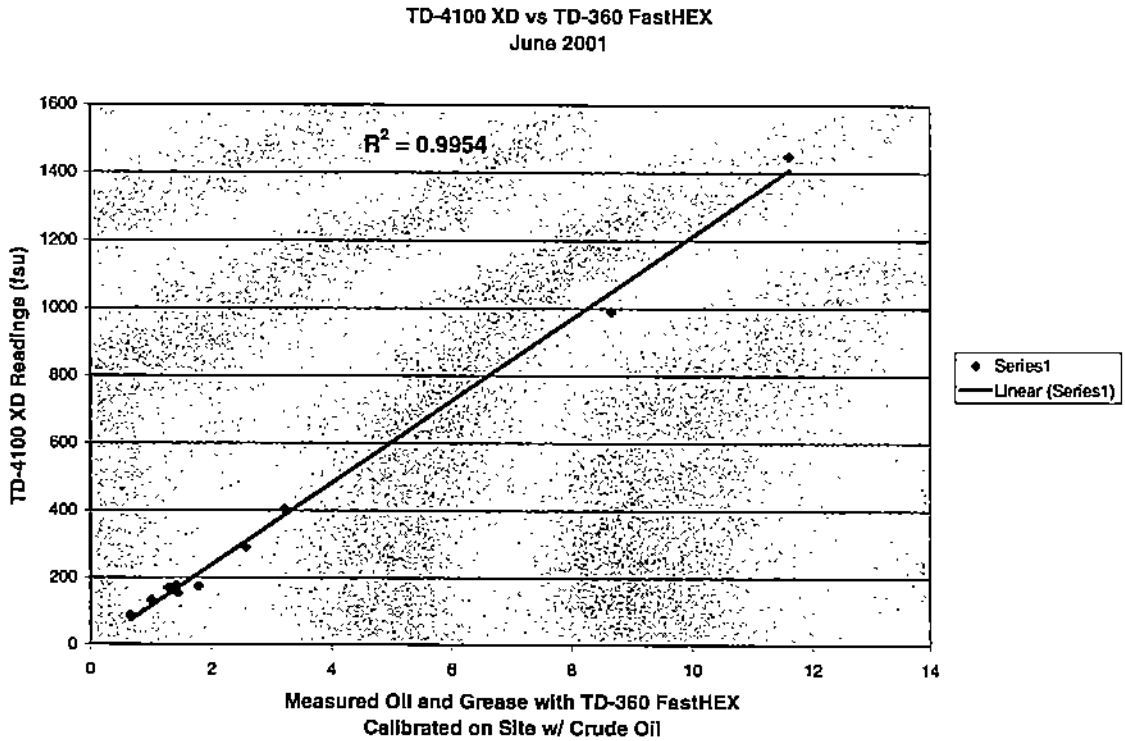


Figure 6

"UV Fluorescence on-line instruments can only monitor totally dissolved oil and not droplets".

If droplets of oil are in the water it seems reasonable that the UV source light would not penetrate the droplets and therefore would not excite all the molecules thereby rendering low emission readings for water containing large amounts of droplets. However, the data does not verify this with the configuration of the TD-4100 XD. The data shows just the opposite. In fact the instrument shows a very linear response to droplets in the water as shown in the data from the bilge monitor certification above and the data below of very high concentration crude oil. In both cases, raw oil was mixed into water and then read directly on the instrument.

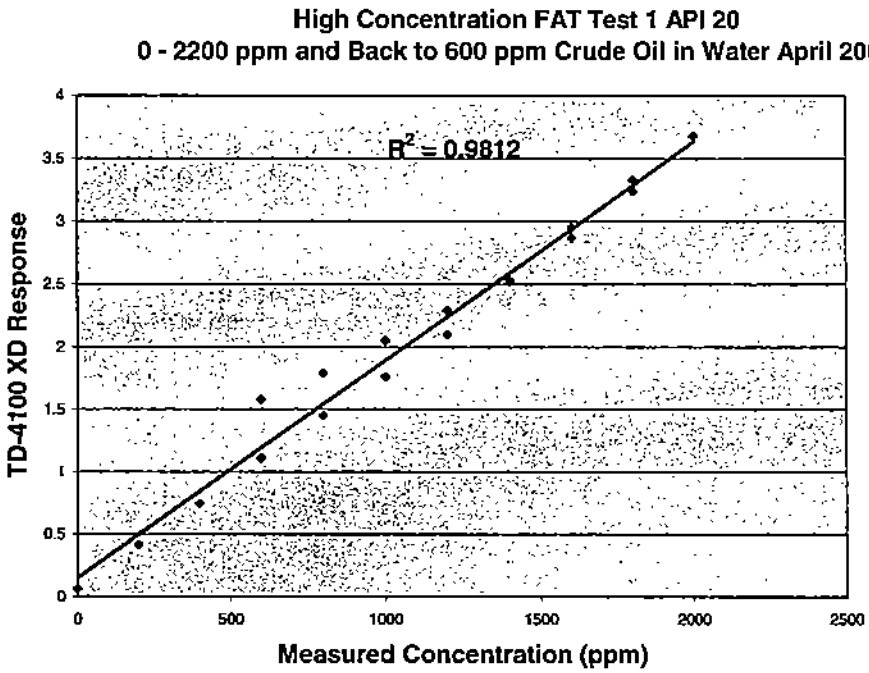


Figure 7

TD-360 FastHEX Data Proves Correlation to Accepted Methods

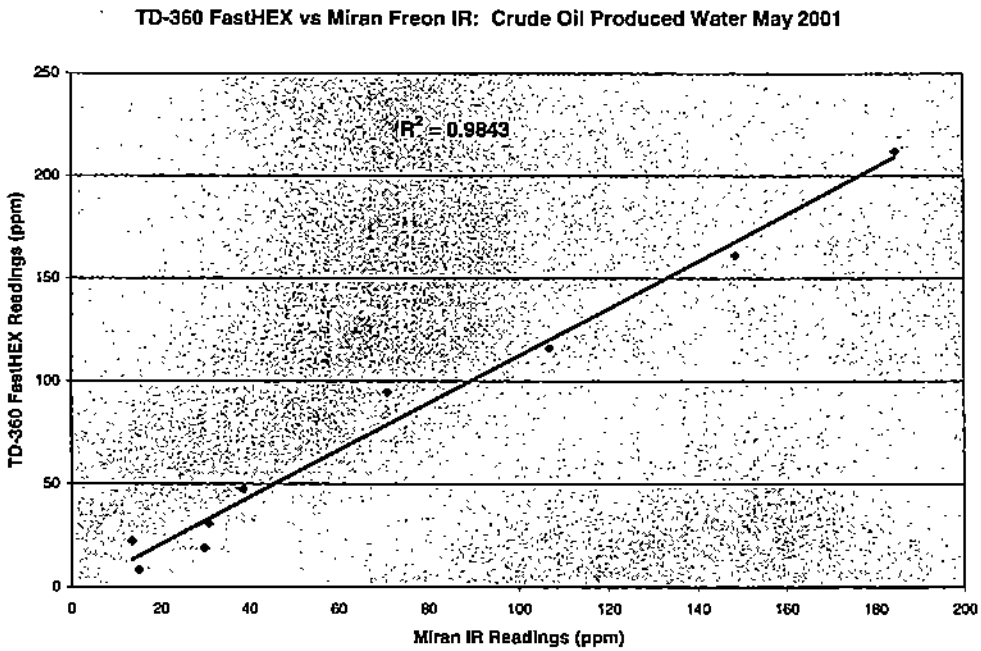


Figure 8

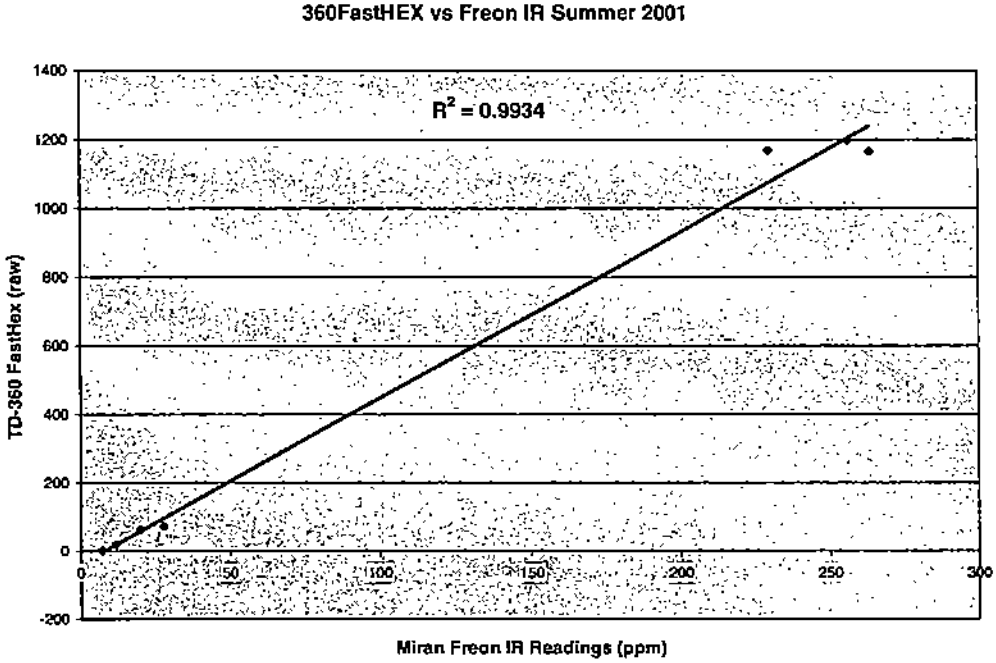


Figure 9

TD-360 Can Use Alternate Solvents

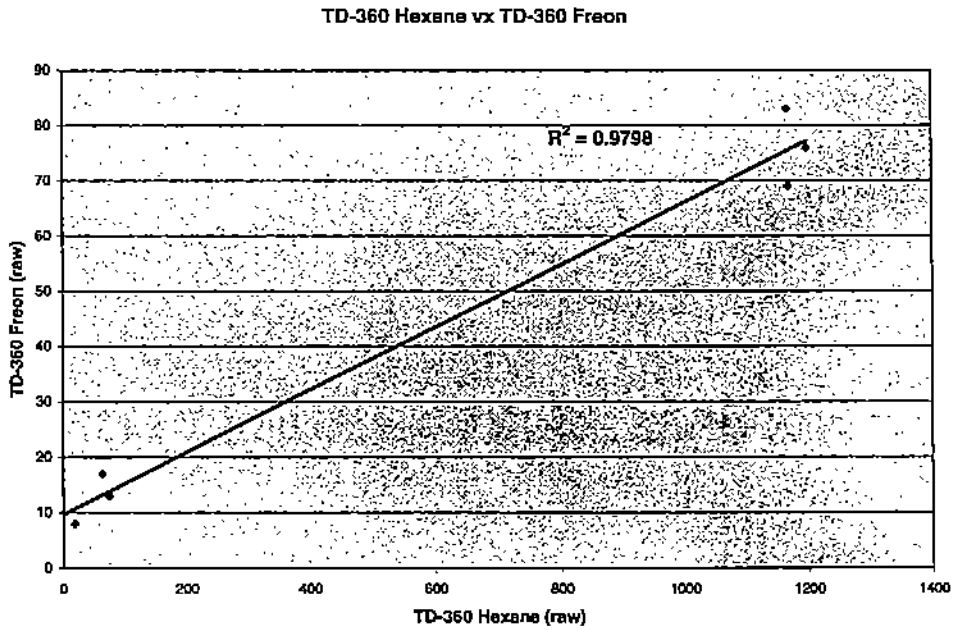


Figure 10

NOTE: Other solvents such as Toluene and Xylene can be used on crude oil applications.

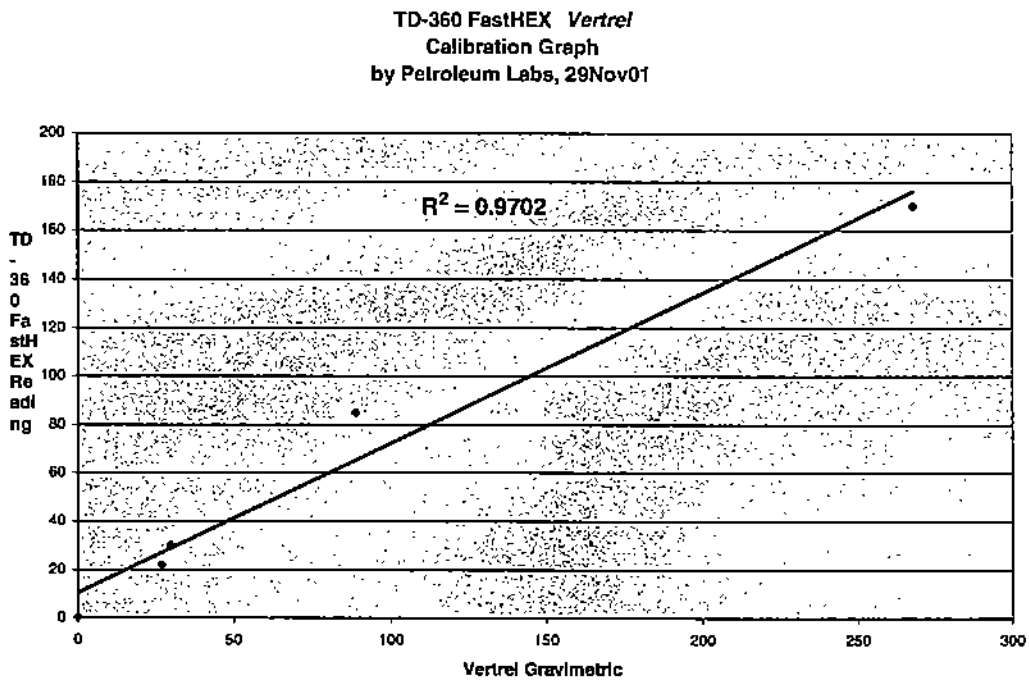

TD-360 FastHEX *Vertrel*
Calibration Graph
by Petroleum Labs, 29Nov01
$R^2 = 0.9702$
TD-360 FastHEX Reading
Vertrel Gravimetric
0
20
40
60
80
100
120
140
160
180
200
0
50
100
150
200
250
300

Figure 11

UVF TECHNOLOGY BACKGROUND

UV Fluorescence Technology

The technological basis for detecting refined petroleum products and crude oil in water is fluorometry. Fluorometers detect and measure materials that fluoresce, usually aromatic hydrocarbons. Petroleum products like diesel, fuel oil and lubricants and many pulp and paper chemicals contain aromatic hydrocarbons.

Fluorescence is a physical process that occurs when a compound, like an aromatic hydrocarbon, absorbs light at one wavelength or energy and spontaneously emits light at a different wavelength or energy. The fluorescence process produces an excitation - emission fingerprint that is unique to each aromatic hydrocarbon, much like humans are uniquely identified by their own fingerprints in a population of people. The primary components of a fluorometer are illustrated in figure 12.

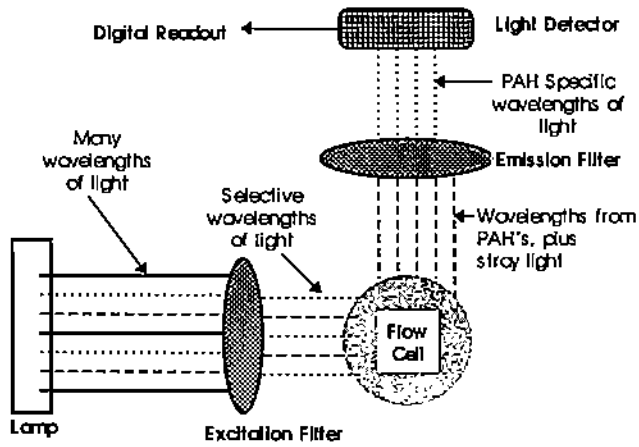


FIGURE 12

The Turner Designs Hydrocarbon Business Group instruments are configured with a matched excitation and emission filter to permit the detection of targeted hydrocarbons, hydrocarbon groups, or hydrocarbon mixtures, while excluding potential interference from scattered light or non-aromatic material.

The measurement of oil and grease is based on the fluorescence signal produced from the class of oils or fuels in the water. The relation to concentration is based either on a direct calibration or a correlation to a laboratory oil and grease measurement method.

UNIQUE ATRIBUTES OF THE TURNER DESIGNS CONTINUOUS ON-LINE MONITORS

Non-Fouling Flow Cell

The TD-4100 / TD-4100 XD incorporates a proprietary non-contact, non-fouling flow cell. This design permits the detection of hydrocarbons in a water stream that falls through an open chamber; the stream does not contact, dirty or foul the optical windows used for monitoring oil in water. A proprietary Air Curtain system

keeps the optical windows fog-free in humid environments or hot water applications. This design has many successful applications at temperatures as high as 190 deg F. This feature is required in any on-line monitoring application where oil is present in water.

There have been several attempts to apply automated measurement cell cleaning systems on full contact instruments and all have failed. These include wiper systems and probe cleaning / washing systems. While no on-line instrument is completely immune to fouling, the TD-4100 and TD-4100 XD have successfully replaced other oil in water monitors in applications where fouling had been a chronic problem. Figure 13 illustrates the falling stream flow cell. This figure shows the sample block as a "cut-away" view, exposing the water stream falling through the open chamber.

Within the flow cell, water falls in an open stream in front of the windows as shown in Figure 13. An inspection port is provided in the front of the Non-Contact Flow Cell. Under normal operation, the falling water is completely laminar and looks like a glass rod. In abnormal conditions, the falling water will be distorted and easily recognizable by the operator. Dirty windows or distorted flow is an indication of blocked or partially blocked sample line. Cleaning of the windows is easily accomplished through the front inspection port.

Within the Non-Contact Flow Cell, the lamp, optical filters, and sensor are all protected from water and contamination by the clear quartz windows. Water does not contact the windows except in highly unusual circumstances such as line plugging and aggressive line cleaning. If water or oil does contact the quartz windows, using the front inspection port, a simple spray of alcohol or detergent followed by a water rinse will bring the instrument back up to operating condition. No further adjustment of the instrument is required.

Aromatic hydrocarbons in the falling water stream fluoresce allowing them to be detected and measured. Each petroleum hydrocarbon has its own unique

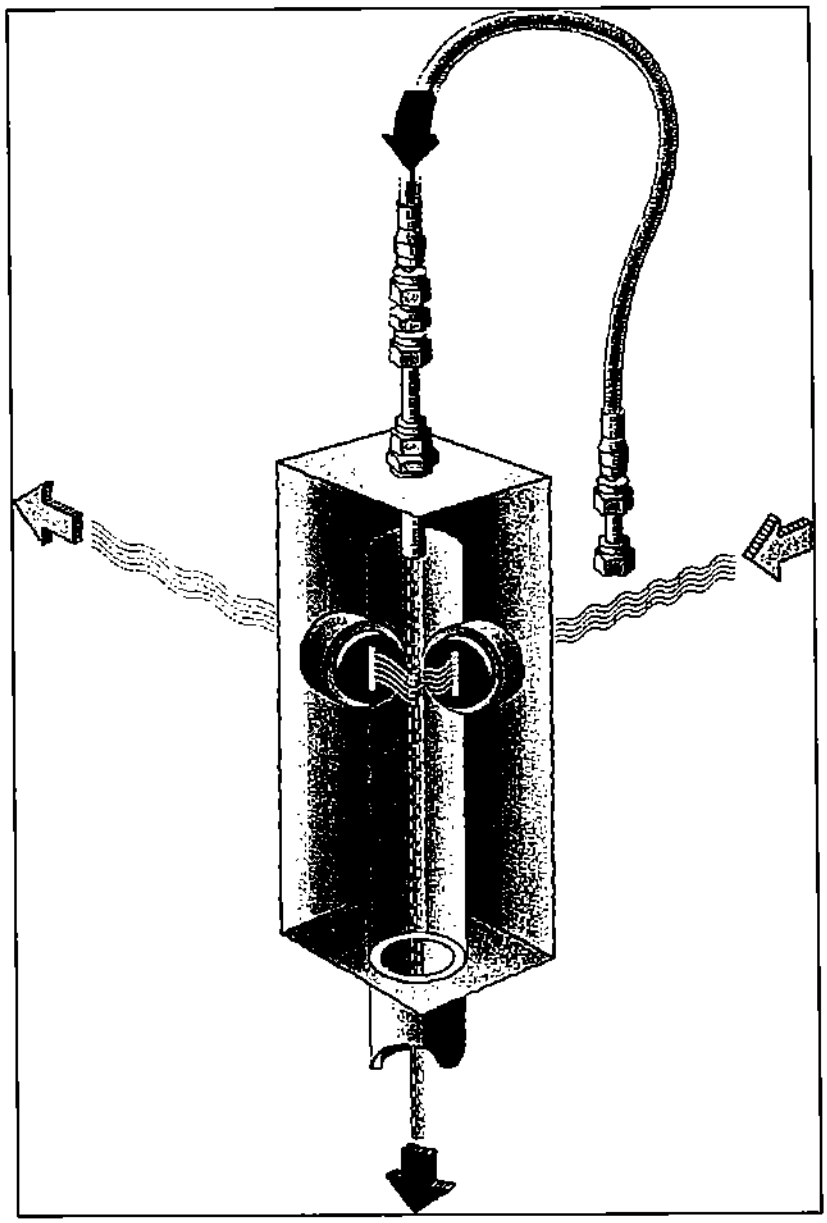


FIGURE 13

wavelength signature. This allows the fluorometer to be specific to the types of compounds when there is enough wavelength separation between the target and potential interference. In other applications, a wide band optical configuration allows monitoring of many target compounds. Turner Designs provides the specific optical configuration for the application by sampling the site water and the target compounds. The minimum detection and linear range of the instrument is matrix and compound specific. For instance, diesel can be monitored at 5 ppb in steam condensate and 20 ppb in some river water, but in other river water the minimum detection limit may be as high as 100 ppb.

Because the fluorometer measures the emitted light from the sample, the detector can be placed at right angles to the source lamp path. See Figure 14. This feature makes fluorescence much less susceptible to changes in signal due to turbidity, color or suspended solids.

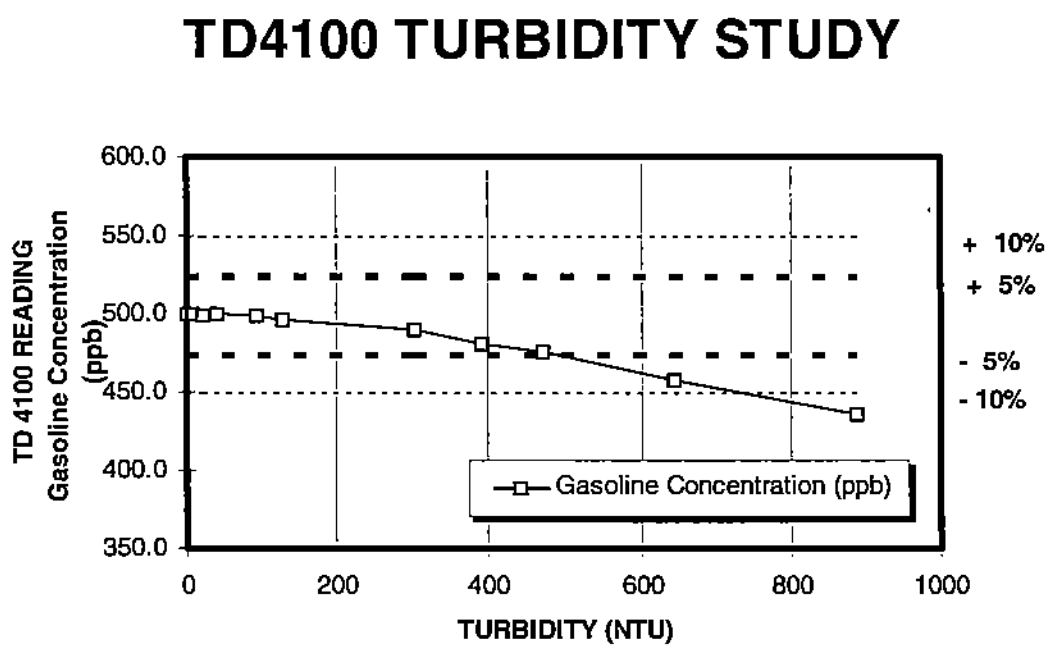


Figure 14. Turbidity Graph

Maintenance of the on-line oil in water monitor

The TD-4100 and TD-4100 XD on-line oil and water monitors are the least maintenance instruments oil in water instruments in the industry. The electronics package is second to none in stability with less than 5% drift in 90 days. (See Figure 15).

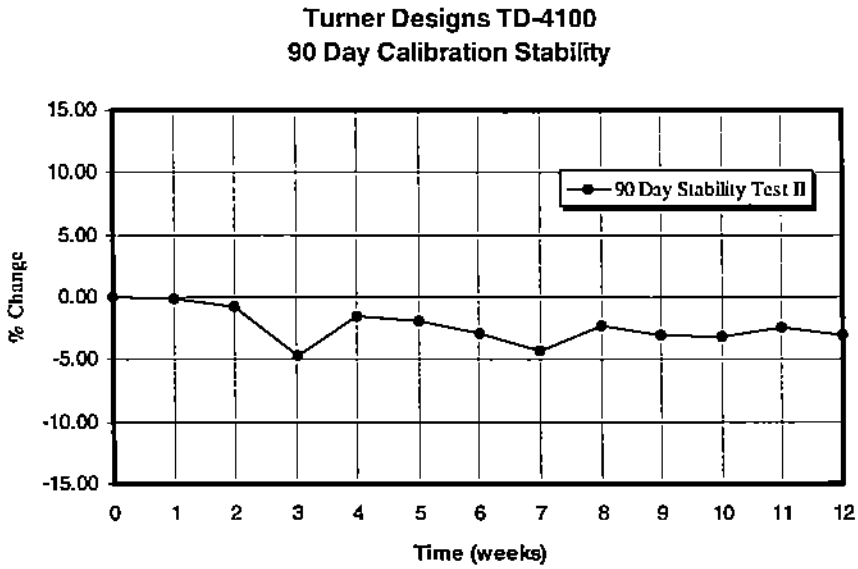


Figure 15 Stability
(50ppb gasoline in water)

Most maintenance issues can be attributed to the sample system. Slugs of oil, bacteria, algae, scale, large solids or intermittent flow conditions all can contribute to higher maintenance. The focus should be on steady state conditions with proper location of the sample probe and prevention of scale or other solids buildup. If steady state flow conditions are not possible, we suggest automated valves be employed to insure proper sample shut down and re-start events. For issues regarding sampling please contact the factory.

References for More Information on UV Fluorescence

1. California EPA Certification with Orignial Data-
   www.turnerdesigns.com/t2/oiwm/oiwm.html

2. IMO / USCG Bilge Water Certification with Original Data -
   www.turnerdesigns.com/t2/oiwm/oiwm.html

3. Ultraviolet Spectoscopy Total Oil Content of Water: Defence Research Establishment Atlantic DREA Contract Report 98/441