

## Monitoring Total Oil Content of Process Wastewater

The experimental results summarized below provide information about the viability of Teledyne's fluorescence based oil-monitoring systems.

Specifically, we explored the ability of the Teledyne unit to monitor the total oil content (0-200 PPM) of wastewater produced during crude oil drilling operations. The monitoring system will be used to ensure that the wastewater generated does not contain a total oil content exceeding the permitted disposal level. The fluorescence-based unit will be used in place of the absorbance based monitoring systems.

In order to describe the experimental results, it is critical to understand how crude oil and water form solutions. In general, only very small quantities (<25 PPM) of crude oil will be completely soluble in produced water. The oil solubility limit is based on the exact chemical composition of the produced water and the temperature and pressure conditions in which the oil and water are mixed.

Oil concentrations exceeding the solubility limit are entrained in the water stream either as suspended droplets (an emulsion) or as a phase separated oil layer. Due to the nature of piping systems, complete phase separation of the species typically does not occur and the produced water stream will most likely be an emulsion. The oil droplet size dispersed in the produced water will vary based on the degree of mixing (shearing) caused by flow conditions in the piping system.

Due to the low solubility of oil in water, measurement of the total oil content requires that the produced water stream must be homogenized, forming a micro-dispersed emulsion. This emulsion will be stable on a time scale sufficient to facilitate optical monitoring.

Figure 1 shows the apparatus used to monitor the test solutions. During testing, the homogenizer was clamped in place and not removed from the solution. The water used in the test series was non-fluorescing ultra high purity water.

EPA #2 oil was used as the mimic for crude oil. Teledyne's Photo-X Fluorometer was operated in Mode 2, which is the most likely operating mode for produced water applications. Mode 2 calibration sets the fluorescence level of the calibration solution at the midpoint of the monitoring scale, 1000 counts. A 200-PPM EPA #2 oil-in-water sample was used as the calibration standard.

The calibration solution and the test solutions were prepared by injecting the EPA #2 oil into 1000 ml of water while homogenization occurred. The Model 6000 Calibration Procedure methods were used to stabilize the solution reservoir and for injection of the oil into the water forming the required solutions.



Figure 1:  
Test apparatus.  
The homogenizer is shown outside the test solution for clarity. During testing, the homogenizer was clamped in place and not removed from the solution.

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Figures 2 and 3 illustrate the experimental results obtained. The 0-300 PPM concentration range was based on a 0-200 PPM application range with the capability monitor concentrations at least 1.5 times the maximum allowed concentration. Figure 2 plots the individual test sequences for comparison.

The variability observed in Figure 2 maybe due to a combination of factors related to fluorescence measurements (primarily temperature affects) or the changeability in the characteristics of oil-in-water emulsions (specifically the size and number density of suspended oil droplets) generated from the same base materials.

Figure 3 combines all the test data and shows a regression analysis. Linear regression analysis of the data is excellent ( $R^2 \sim 0.97$ ), and a second order regression only marginally improves the data fit ( $R^2 \sim 0.99$ ). Clearly, the results indicate that the fluorescence unit is capable of monitoring the total oil content in the test samples.

Figures 4 and 5 show the same 200 PPM oil-in-water sample immediately after homogenization and after sitting overnight.

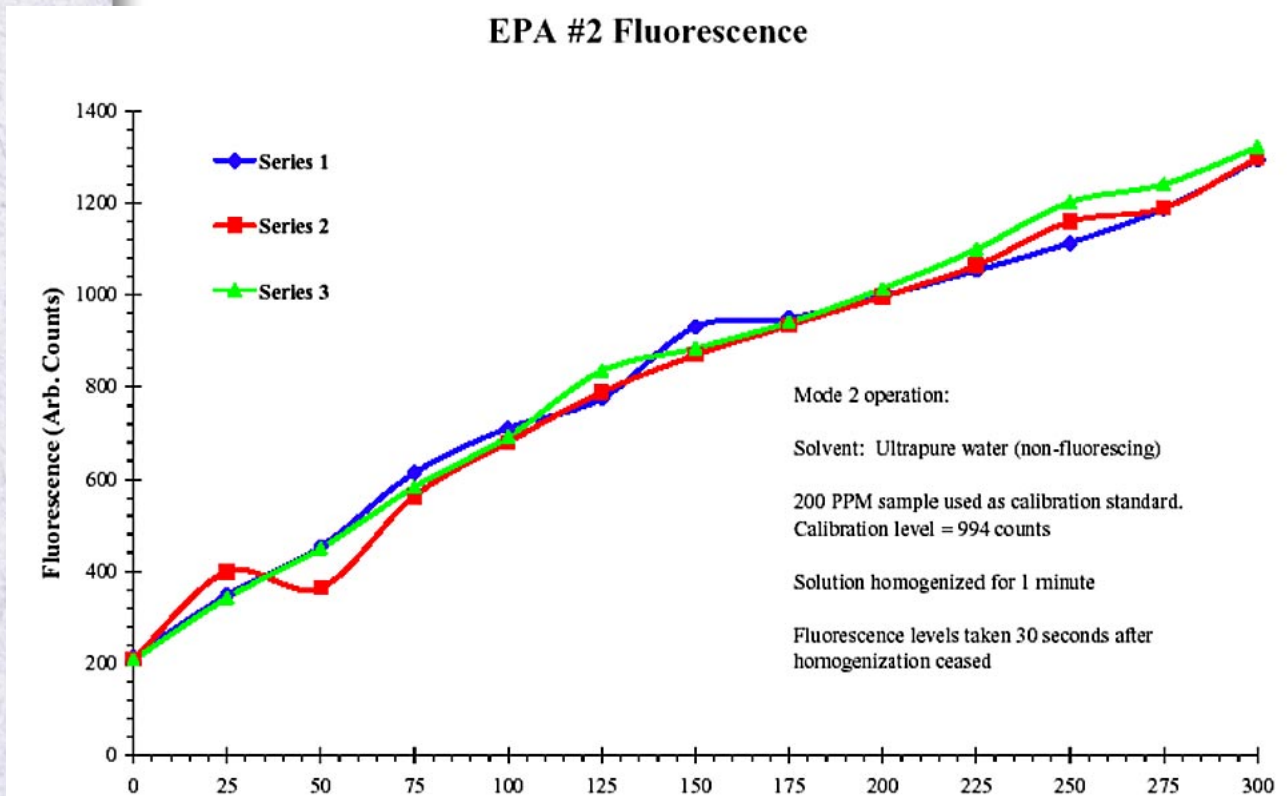


Figure 2: Comparison of the experimental data from three test sequences. The data was acquired over a three day period with only one instrument calibration.

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## EPA #2 Fluorescence

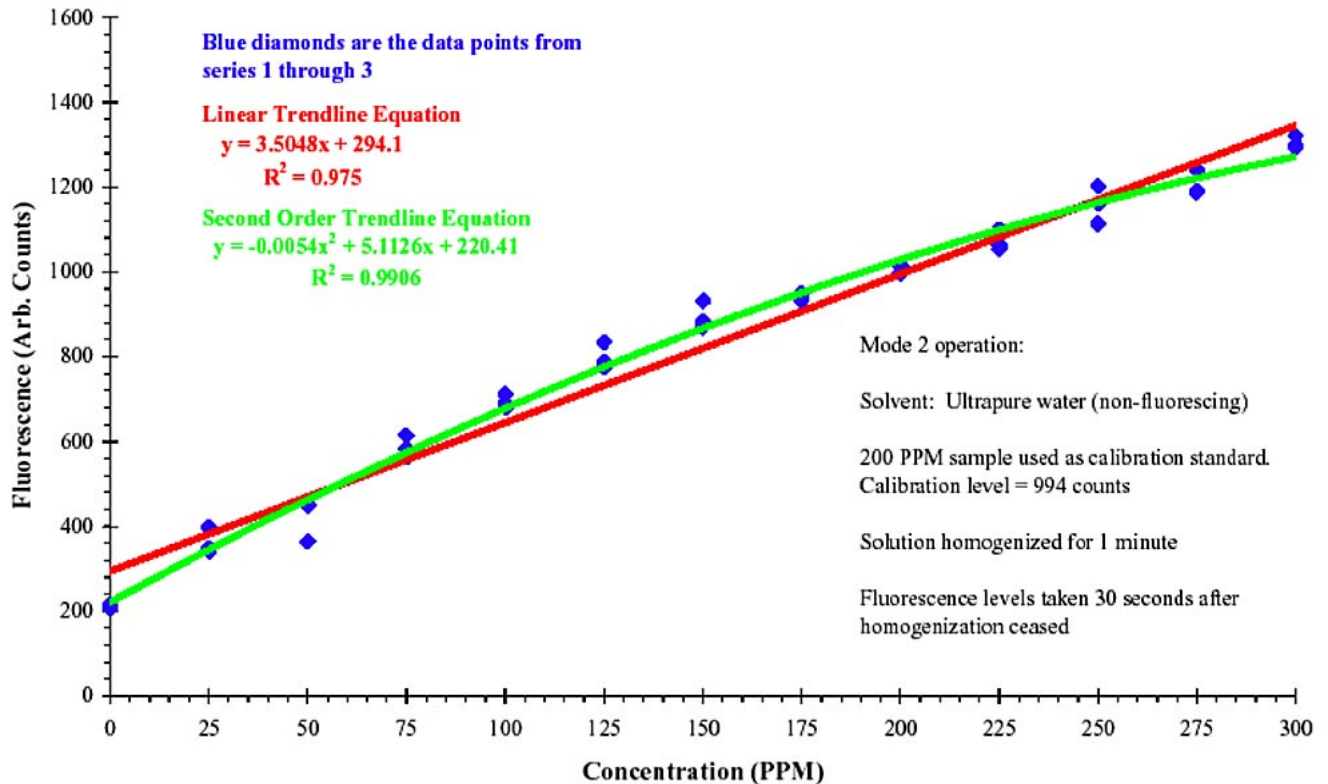


Figure 3: Regression analysis of the experimental test data. The raw data (blue diamonds) plotted is the same data as shown in Figure 2. The colored text for the regression analysis parameters corresponds to the same color trend line in the chart.

Clearly, the solutions appear very similar. After sitting overnight, however, there was a sheen of phase-separated hydrocarbons on the water surface. No hydrocarbon sheen was observed after homogenization or after the short 30 second wait before the fluorescence levels were recorded. In fact, the hydrocarbon sheen was not observed until about 4 minutes after homogenization ceased.

In conclusion, the laboratory analysis of the EPA #2 oil-in-water samples indicates that fluorescence monitoring of the total oil content is a viable application for our hardware. The monitoring system will require Mode 2 calibration using a

laboratory prepared standard solution with the maximum allowed oil content.

The standard solution must be prepared from the specific crude oil and produced water to be monitored. Since the maximum oil concentration exceeds the solubility limit of the produced water, homogenization of the sample is required to insure the accurate determination of the total oil concentration. While only the 0-200 PPM total oil range was examined, there is no reason to believe that the unit will not work for any oil concentration range desired.



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Figure 4: 200 PPM of EPA #2 oil homogenized for 1 minute.

Note: It is important to note that even in this stabilized emulsion the readings were very predictable. This shows the advantage of the front surface fluorescence probe.

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Figure 5: Solution from Figure 4 allowed to stand overnight (~18 hours). There was a sheen of hydrocarbon on the water surface.

## Conceptual Description of Hardware Required:

Teledyne provides a turn-key, oil-in-water, UV Photo-X fluorometer system, which can be integrated with Teledyne's sample handling system. The optical configuration should allow the unit to monitor for a wide range of crude oil compositions. However, each specific crude oil application should be reviewed by Teledyne personnel to ensure the optical configuration is acceptable.

The system will be composed of a UV Photo-X Fluorometer and a process compatible fluorescence probe and monitoring cell. The monitoring cell is required so that the fluorescence unit can be combined with the existing sampling system. The monitoring cell will be constructed of either an engineering polymer compatible with steam cleaning or a suitable material compatible with the required solvent cleaning process. The monitoring cell will be designed so that pneumatic or manual valves can isolate the cell from the sample system and admit the cleaning agent. Additionally, the monitoring cell will be designed to minimize the required sample volume while maintaining the required fluorescence monitoring conditions of minimal stray light and minimal light reflection from surfaces in the sampling volume.

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## Warranty

Instrument is warranted for 1 year against defects in material or workmanship. NOTE: Specifications and features will vary with application. The above are established and validated during design, but are not to be construed as test criteria for every product. All specifications and features are subject to change without notice.

