



## **A new, self-cleaning continuous on-line oil-in water analyzer for the petroleum industry**

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### **Introduction**

The oil and gas industry produces much more water than petroleum hydrocarbons. This water is usually injected back into the underground reservoirs for pressure support and secondary recovery by water-flooding. In some instance, produced waters are discharged overboard from producing platforms into the ocean. Although the water is treated by various means to recover the maximum amount of hydrocarbons, traces remain that are too difficult or costly to completely remove. Most countries now limit the amount of oil and grease (O&G) or total petroleum hydrocarbons (TPH) that may be discharged to the environment. These limits protect the ocean's toxicity and from forming unwanted visible sheens on the surface. Operators are required to treat the produced water to the discharge limits and to monitor the concentrations of O&G or TPH that are released. These measurements not only provide the operator with information on hydrocarbon releases to the environment, but also are useful in monitoring water treatment processes and management of this fluid that is produced and handled at much higher rates than the hydrocarbons themselves.

A variety of analytical methods have been developed to monitor the O&G or TPH in produced water. Some of the more common methods currently utilized for monitoring hydrocarbons in water include gravimetry, ultraviolet-visible (UV-vis), infrared (IR), and fluorescence (FS) spectrometry. Newer methods now being contemplated for monitoring TPH in produced water consist of gas chromatography. In the UV-vis, IR and FS methods, O&G or TPH is extracted from the water with solvents. The solvents may be toxic, harmful to stratospheric ozone, etc. Currently, significant efforts are being made to eliminate the use of these solvents, their contact with personnel, and their method of disposal.



In order to reduce labor and solvent use required for water grab sample analyses, a number of vendors have introduced on-line monitors to allow faster response and feedback to operators of water treatment processes. Some of the monitors are completely continuous; others are intermittent. While these monitors have certainly reduced the amount of solvents used in extraction processes, and have reduced chemical technician time in grabbing “snapshot” samples of TPH in produced waters, they have encountered some drawbacks. Optics or other equipment directly exposed to the water in these on-line monitors may foul with emulsions or solids. In certain oil production facilities, these monitors have required excessive maintenance by operators to prevent fouling. Eventually, operators tire of the constant maintenance required, and eventually shut the units down so as to rely solely on the chemical technician to conduct the grab samples for analysis.

Chevron Corporation has been searching for alternatives to continuous oil-in-water (OIW) monitors that may be easier to maintain and operate than existing units. In the one field, OIW monitors for overboard discharge are easily fouled with precipitates that are generated to prevent the release of soluble metals into the ocean. The precipitates are sometime quite “sticky” to glass optics in these on-line OIW monitors, requiring constant maintenance by operators. In another field, sodium carboxylate soaps/emulsions foul the optics of existing OIW monitors.

As a result of these fouling problems, a project was initiated to search for improved OIW monitors that would be self-cleaning. This would reduce operator maintenance, cleaning, excessive calibrating, and constant “grabbing” of samples to monitor overboard water quality. We investigated several new OIW monitors that were claimed to be on-line, continuous-reading and self-cleaning. The latter feature was deemed most critical to encourage operations to monitor TPH from control panels and not to turn off the monitors when they began requiring frequent mechanical cleaning and re-calibration. The study was designed to determine if new generations of OIW monitors could improve operations through alarms and trend analyses. Whilst the desired monitor was not expect to be used for reporting TPH discharges to regulators, “early-warning” of water treatment problems could be useful to prevent O&G releases and sheens. The optimum monitor would not replace “grab samples” for regulatory reporting, but to assist operations in reducing unwanted releases of hydrocarbons and to meet corporate responsibilities of environmental protection.

Three different self-cleaning, continuous, in-line monitors were identified as the most promising for meeting the objectives of this study. One had already been installed at a Chevron facility. It was developed jointly with seed funding from a Unocal Corporation business unit. Although that monitor has performed well, the vendor has not been able support other business units outside of its local sphere of influence. Therefore, two Advanced Sensors’ EX-100 OIW monitor units were installed in the Gulf of Thailand; one on Tantawan field FPSO and another on Benchamas field FSO. The commissioning of the unit on the former overboard water discharge line was achieved in December 2006 without incident. In contrast, the latter unit installation was interrupted by a typhoon warning evacuation. It was later discovered that the original EX-100 unit on Benchamas FSO experienced interferences due to the injection of a demulsifier chemical into the water during oil-water separation operations. The EX-100 unit was upgraded to an EX-1000 unit to overcome the interference. The unit on Tantawan has performed well since early December 2006 without the need of any human intervention, maintenance or cleaning.

### **Measurement Technique**

The measurement technique incorporated in the Advanced Sensor’s monitors is laser induced fluorescence. The transducer sensor head is a patented, combined Optical and Ultrasonic component. Water passes through a measurement chamber (300mL), within the chamber there is a small sapphire window used for measurement and a larger sapphire window for viewing the inside of the chamber. The laser passes through a smaller sapphire window to excite the water sample, the fluorescent properties are captured via Optical fibre light guides and taken to :

- An optical filter and photo multiplier tube (PMT), the optical filter selected depends on the wavelength properties in the water.
- And an optical UV spectrometer (for the EX1000)

Fig. 1 below shows a simplified schematic of the Advanced Sensors' self-cleaning, continuous, on-line OIW monitor.

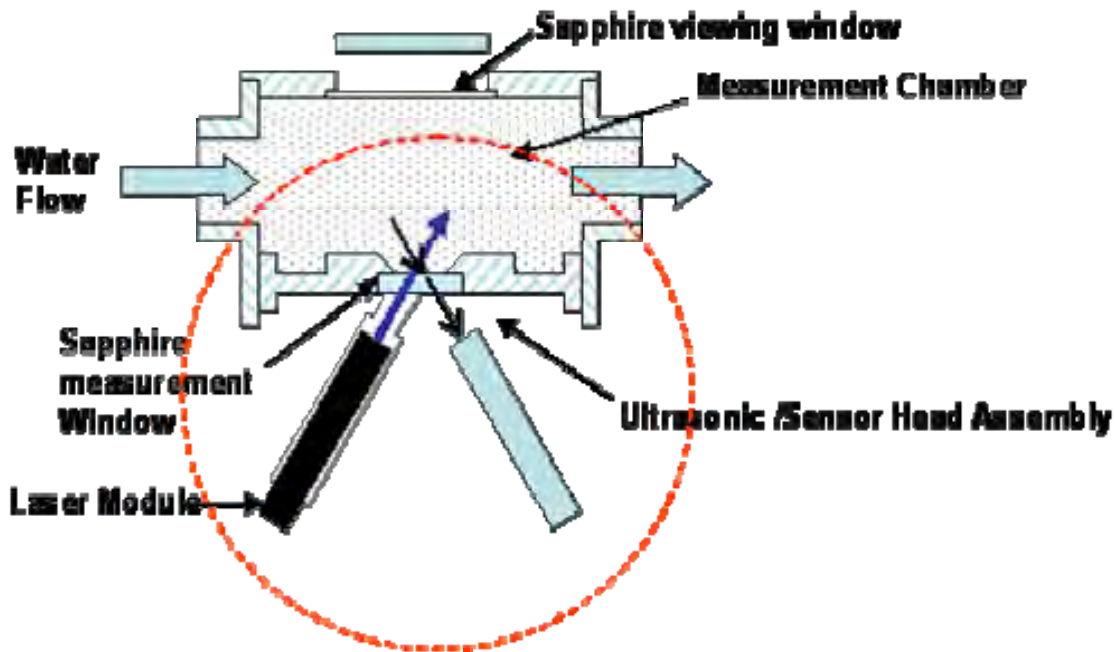


Fig. 1. OIW monitor schematic

### Ultrasonics

The Ultrasonic transducer performs 2 functions:

- It cleans the sapphire windows ensuring that measurements do not deteriorate.
- It periodically homogenizes the sample to correct for oil droplet size variation

### Spectrometer

The in-built UV spectrometer (EX1000 only) scans the water every 10 minutes and files the results for 10 years for future investigation. The spectrometer is of great value when detailed analysis of water content is required. An installed unit was periodically reporting higher OIW concentration results than the field laboratory that used solvent extraction and IR detection. The spectrometer logs were examined during this event, and the spectra indicated the presence in the water of an interferent other than oil. Further tests were performed, and the substance causing the anomaly was identified. This led to the selection of a new wavelength range and an optical filter that was fitted to the PMT, thereby eliminating the interference (see Fig. 2 below).

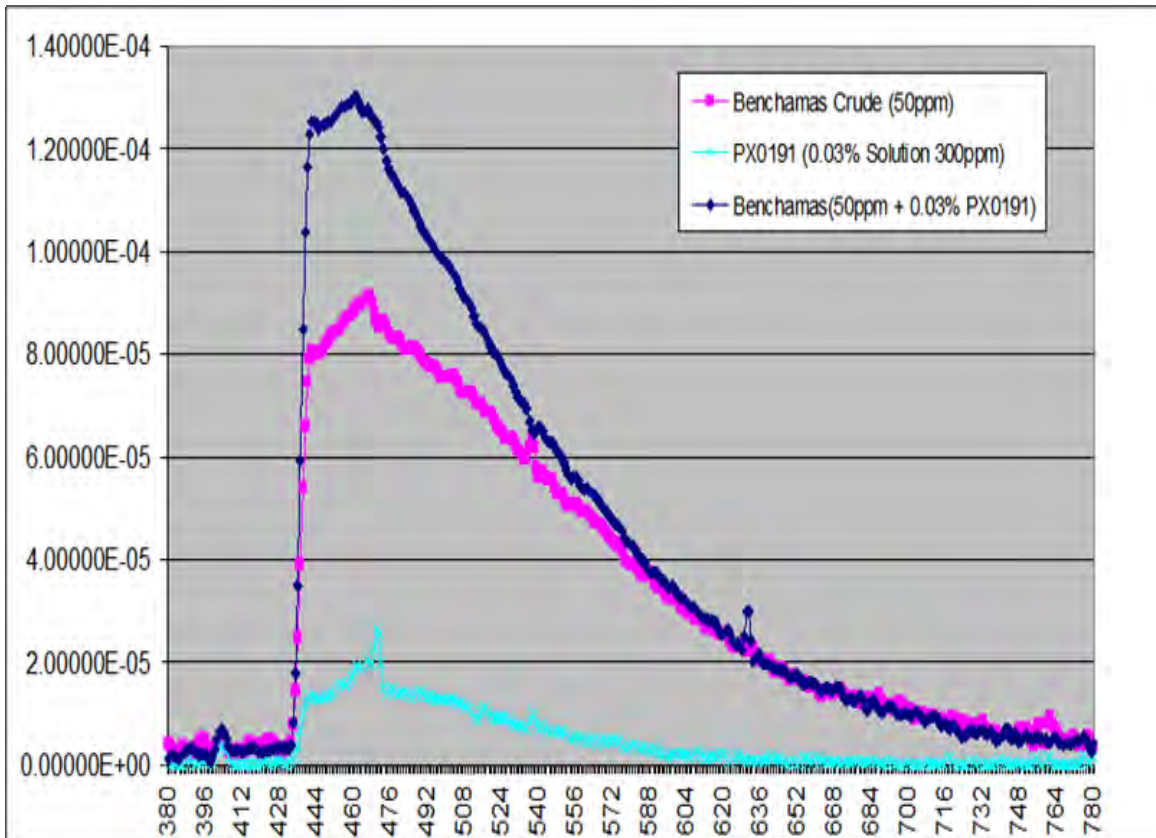


Fig. 2. Spectrophotometric scan of water, chemical and chemically-treated water (y-axis intensity; x-axis wavelength, nm).

Whilst chemicals can be evaluated in the Advanced Sensors Laboratory and isolated before the monitors are delivered, the in-built spectrometer facilitates the evaluation and analysis of new chemicals or additives being introduced to the process.

### Operating dynamic range

The dynamic range of most OIW monitors is limited to 500 ppm or a maximum of 1000 ppm TPH. The standard EX100/1000 can operate up to 3,000 ppm TPH. The “EX1000Advance” has a direct fluorescent dynamic range of 20,000 ppm OIW without any extrapolation. See below in Fig. 3, the direct fluorescent curve for 0 to 30,000 ppm OIW without any extrapolation. After 20,000 ppm, the instrument flat-lines. The flat-lining in itself is a new development, traditionally as oil levels increase the fluorescence flat-lines and then falls, this can confuse an instrument in believing the oil content is falling when it is actually rising. The extended range monitor “EX1000Advance” facilitates the monitoring the efficiency of separators and hydro-cyclones, providing a greater insight to process dynamics.

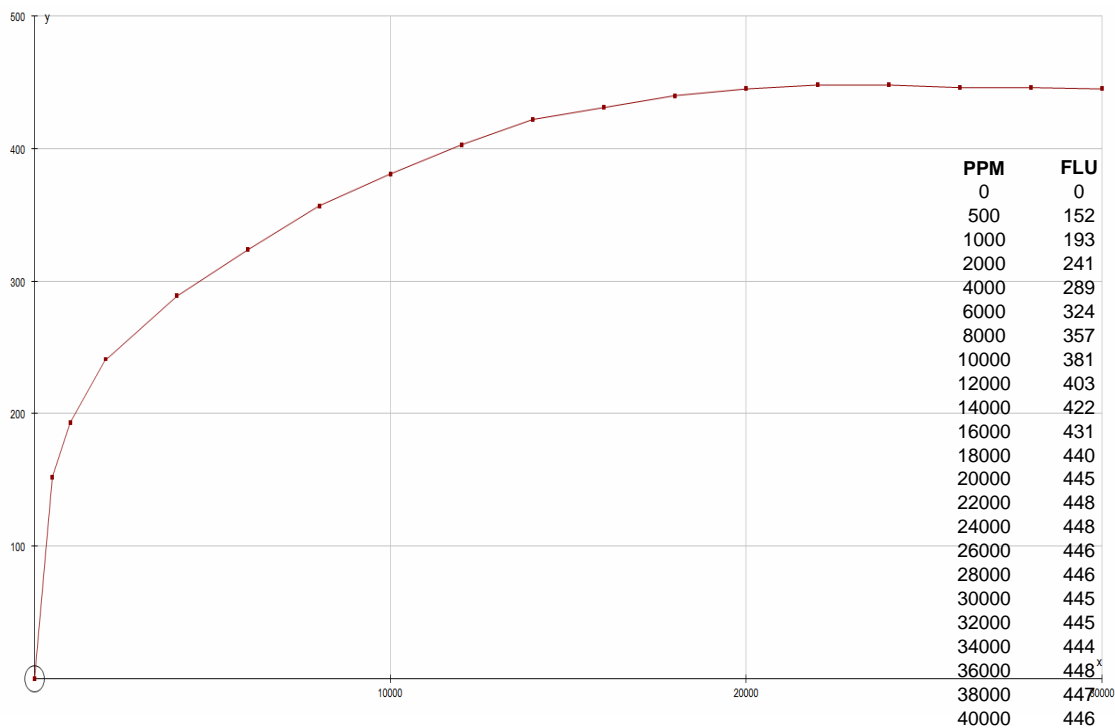


Fig. 3. Fluorescence scan

### Operating History

After installation of the EX-100 and EX-1000 on the produced water discharge pipelines in the Gulf of Thailand fields, laboratory “grab” samples were compared with output data from the OIW monitors. The results of this comparison show remarkable agreement between the extraction/IR method and the Advanced Sensors’ monitors (see Figs. 4 and 5). Furthermore, with a little fine tuning and a slightly improved process in taking and analyzing the laboratory samples, even better agreement has been achieved.

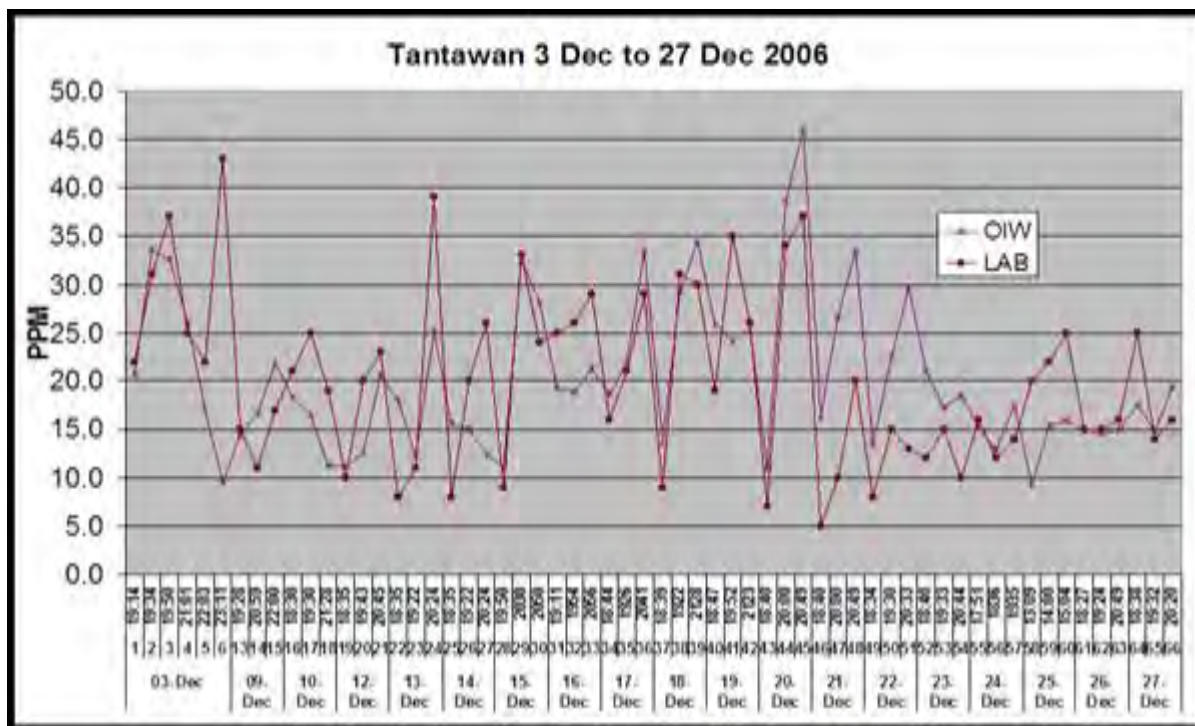


Fig. 4. Tantawan FPSO Produced Water Discharge: EX-100

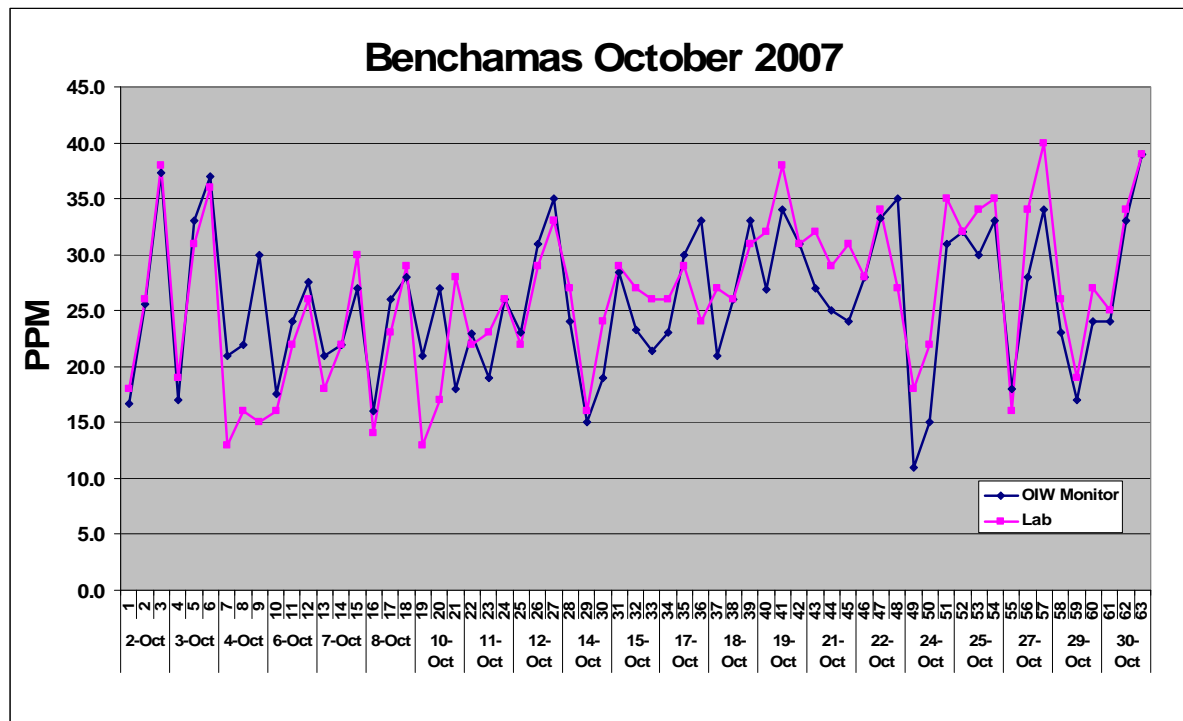
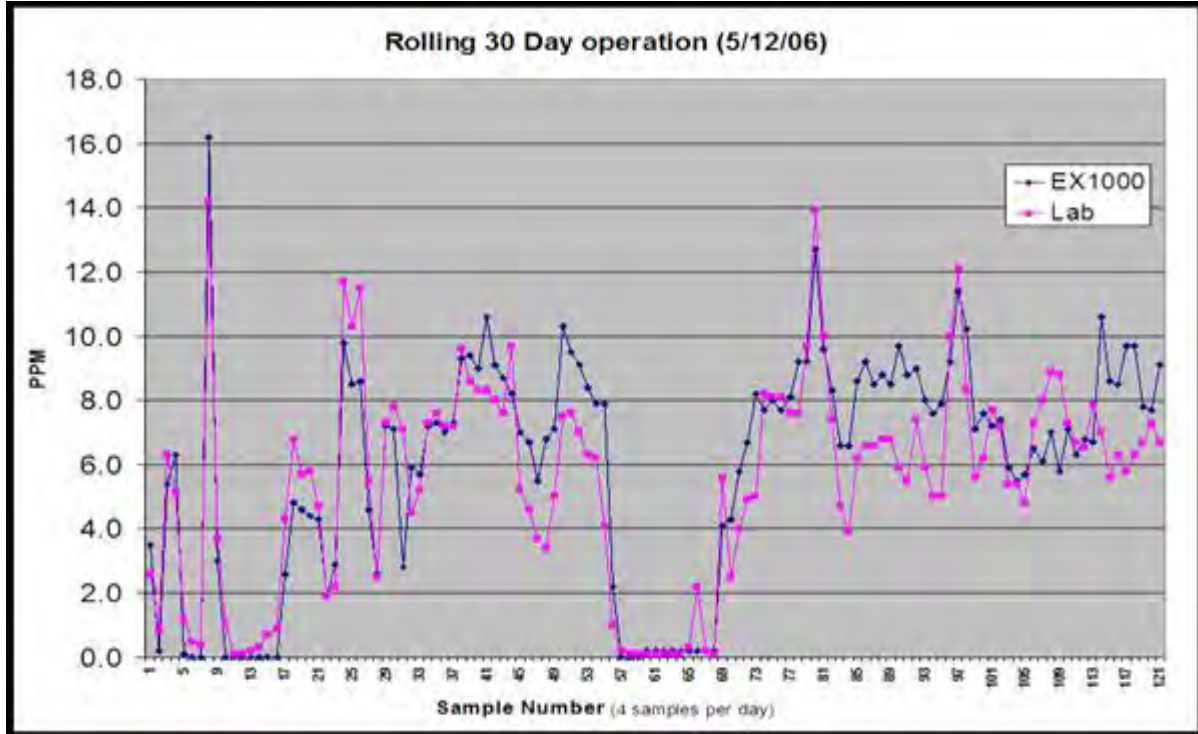


Fig. 5. Benchamas FPSO Produced Water Discharge: EX-1000



Fig. 6 compares the results of laboratory OIW analyses with an EX1000 unit located at an oil terminal. Generally, good correlations are achieved between the terminal's EX-1000 unit and laboratory measurements by extraction and infra-red detection.



## Conclusions

The Advanced Sensors' OIW monitors are continuous, on-line, self-cleaning UV fluorescence detection systems. Advantages of this laser fluorescence system for monitoring OIW are many:

- Instead of the laser or light source having to pass across a pipe to a detector, the requirement to completely flow photons through moving water is eliminated.
- With the Advanced Sensors' flow through cell, the light source and detector with the specially coated sapphire window detects all TPH or O&G in the chamber. The ultrasonic beam not only homogenizes the sample in the chamber, but also cleans the sapphire window. In the presence of "sticky" precipitates or from soapy emulsions, ultrasonics maintains a clean window. In the homogenization zone, and when the chamber is briefly closed, the powerful sonication churns up the oil into a homogeneous mixture with a relatively uniform standard droplet size distribution. This eliminates the need for particle or droplet counting in water systems where fluids may be highly variable in composition, quality and flow rate.
- The Advanced Sensors' technology is able to cope with system upsets, well flow variations, and solids. The homogenization mode is especially applicable to sour systems where oil-coated iron sulfide solids may be present in suspension or in emulsions.



- For each application of this technology, UV fluorescence signatures may be obtained so that the bandwidth is specific only to dispersed oil. When chemical additives are present that overlap with the oil bandwidth, Advanced Sensors' professionals are able to remotely squeeze the bandwidth tighter to ensure that the output signal is focused on oil alone.
- The standard communication interfaces are 4-20mA, Ethernet and ADSL (2 wire Ethernet), wireless is available as an option. The 4-20mA is for connection to the Control room (DCS) and the Ethernet and ADSL is for connection to the company's intranet. The intranet/internet connection facilitates the connectivity to the instrument from other company locations or the advanced sensors laboratory for further diagnostic and analysis support.
- Data logs. PPM measurements are stored every second in daily logs as excel files, the daily logs are stored for 10 year on the instrument. The spectrometer's scans are run every 10 minutes and excel logs are also stored for 10years on the instrument. Software is provided to interrogate both data logs (LogView) and Spectrometer Logs (Span). Both LogView and Span can be utilized remotely, the software will reach down to the Monitor and extract the selected filed for investigation
- Alarm levels may be set for trending or operator attention to the water treatment and processing system.
- The unit can also manage multiple streams to the instrument, controlling a valve on each stream. Each steam can be easily scheduled in order and duration of flow.