

## **USE OF PHOTO-ACOUSTIC MEASUREMENT TECHNOLOGY TO MEASURE HYDROCARBON CONCENTRATION LEVELS IN RE-INJECTION LINES**

**P. Terzoudi, Flow Measurement Group, Kvaerner Oilfield Products Ltd  
T. Whitaker, Flow Measurement Group, Kvaerner Oilfield Products Ltd  
H. A. Mackenzie, Department of Physics, Heriot-Watt University**

---

### **ABSTRACT**

This paper describes the use of photo-acoustic measurement to determine the Ppm concentration of hydrocarbon in water re-injection pipelines. The basic techniques are described, with reference to the impact of pressure, temperature, salinity and background noise levels on the precision of the measurement. Data from laboratory and field trials of a production prototype instrument will be presented to indicate the quality and reliability of measurement, which can be obtained, based on data acquired during an ongoing development project.

### **1 INTRODUCTION**

In the field of environmental monitoring there is increasing interest in the monitoring of hydrocarbons, which may be found in the marine environment as pollutants from the offshore oil-production process. Produced water is a by-product of crude oil production, which is either discharged over board from offshore installations or is re-injected into the crude oil reservoir, and is obtained from two main sources: seawater injected into the reservoir during oil production processes and naturally occurring reservoir formation water. Produced water is known to contain varying concentrations of crude oil, production chemicals, solids and gases, and its disposal introduces environmental, operational, and economic considerations. A current interest in offshore oil production is towards subsea facilities that utilise the re-injection of produced water.

This offers both environmental advantages because it avoids the disposal into the sea and economic benefits because it extends the cost-effective lifetime of established fields and allows exploration and production in more inhospitable regions.

The analysis of the hydrocarbons using near infra red (NIR) transmission spectroscopy requires pre-treatment of samples and is further complicated by the presence of the background absorption of water in this spectral region. Although these difficulties may be overcome in the laboratory environment, the technique of transmission spectroscopy does not transfer successfully into industrial on-line measurement requirements. As an alternative approach, a pulsed photo-acoustic (PA) monitoring system has been developed, which permits the routine spectroscopy of hydrocarbons concentrations in produced water, without special sample preparation. This application involves the deployment of sensor heads directly into the produced water pipelines.

Historically, Photo-acoustic techniques have a wide range of applications in other industries from the analysis of semiconductor materials to atmospheric monitoring, and successful transfer to the oil and gas industry should be straight forward.

## 2 PRINCIPLE OF OPERATION

Basic photo-acoustic spectroscopy uses sealed cells and conventional light sources with mechanical chopping to modulate incident light which, via optical absorption and resultant heating, caused detectable bulk expansion of the sample. Pulsed photo-acoustic spectroscopy relies on the measurement of the amplitude of an optically generated acoustic pressure wave. When a pulse of light is fired into the medium and selectively absorbed by a molecular system, the non-radiative energy generates a temperature rise causing expansion, resulting in the generation of an ultrasonic pressure wave. The magnitude of the pressure pulse to a first approximation is proportional to the optical energy pulse, the optical absorption coefficient, the linear thermal expansion coefficient, the velocity of sound in the medium, the specific heat at constant temperature and the acoustic source radius. In practice however, the photo-acoustic signal amplitude is normalised by dividing the signal amplitude by the laser pulse energy to give the term PA/E so that, from the wavelength dependence of the optical absorption, a photo-acoustic spectrum is generated. The photo-acoustic spectrum has the same primary features as the transmission spectra, but the magnitudes of the spectroscopic features are dependent on the combination of the physical parameters mentioned above.

## 3 THE PHOTOACOUSTIC SYSTEM

### 3.1 General System Operation

Commercially available diode lasers have been utilised as low-cost, reliable, and compact optical sources for pulsed photo-acoustic generation. Typically lasers with an emission wavelength of 905 nm have been incorporated. This wavelength is particularly useful due to the relative optical absorption coefficients of crude oil and water, typically  $14.8$  and  $0.4 \text{ cm}^{-1}$ , respectively, at this wavelength. The diode lasers utilised provide output pulse energies in the order of  $1\mu\text{J}$  and pulse widths of  $\leq 100\text{ns}$  Fig. 1 (full width half maximum). Such devices require large transient current pulses (typically  $\sim 40\text{A}$ ) and commercially available current pulse driver units have been used in the present system. For operational convenience, fiber optics have been utilised for optical delivery of the laser output to the sensor head. Due to the large emitting region of the diode laser (typically  $400 \times 340\mu\text{m}$ ) and associated divergences, a high numerical aperture (0.37) (core/cladding) multimode optical fiber has been utilised along with a combination of imaging lenses for efficient laser/fiber coupling.

To detect the photo-acoustic pressure pulses, which are typically  $\leq 1\text{Pa}$ , sensitive acoustic transducers have been incorporated into the system sensor head. To achieve the required sensitivity and to satisfy the operational conditions piezoelectric ceramics have been utilised. To improve the sensitivity of the acoustic detection, the thickness of the ceramic was selected such that the rise time was equivalent to the temporal width of the compressive component of the bipolar acoustic pulse. The sensitivity was further enhanced by increasing the device area and this required the matching of the transducer geometry to that of the pressure pulse, such that segments of the piezoelectric were utilised to intercept the propagating acoustic pressure pulses.

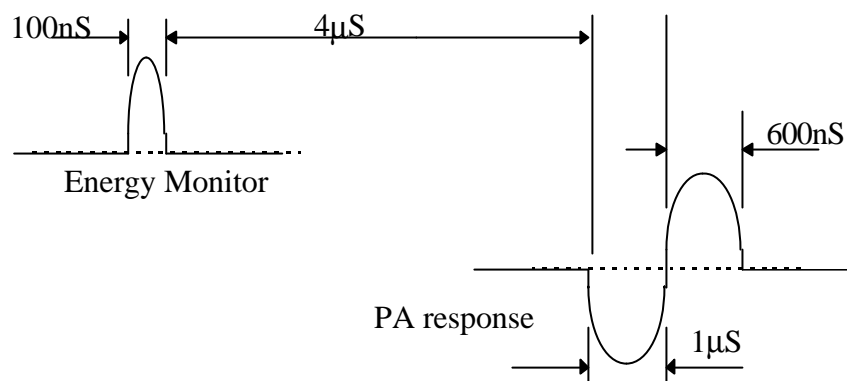
The laser fires pulses of light through a sapphire window into the fluid. A Piezo-Electric Acoustic Transducer (**PZT**) detects the resulting response, which is termed the **PA** response. The photo-acoustic pulse generated a transducer signal of the order of microvolts.

The transducer signal is in turn amplified to achieve optimum input to the analogue-to digital (A/D) sampling card for data analysis and manipulation. Since the acoustic pressures are generally in the ultrasonic range, the accurate measurement of the transducer signals requires fast A/D conversion and a computer plug-in card with 8 bit resolution has been utilised.

In order to confirm the energy delivered in the laser pulse is consistent, a beam splitter was used to reflect a small proportion of the light and a photodiode converts this to an electronic pulse, which is termed the **Energy Monitor**. The data acquisition card also acquires the signals from the photodiode, which is incorporated to determine and compensate for

variations in the optical energy output from the nominally stable diode laser source. The photodiode signal from the reflected optical pulse (from the beam-splitter) is digitised at the same sampling rate as the photo-acoustic signal. These energy monitor signals were found to be directly related to the optical energy incident on the samples. The magnitude of the acoustic pressure pulse is proportional to the incident optical energies, such that normalising this to the optical energy should compensate for any variations. In practice this is achieved from the ratio of the peak-to-peak value of the acquired transducer voltage signal, and the magnitude of the photodiode signal; this ratio provides a constant value over a range of optical energies.

The height of the PA response peak indicates the strength of the PA response and therefore how much oil is in the water.



**Figure 1 - Oil in Water Monitor Energy Monitor and PA Signals**

Noise is associated with all the physical measurements and it is important to characterise the overall instrumental performance. This was done by applying the standard data technique of signal averaging. Typically, a set of 1500 successive photo-acoustic signals were acquired and averaged in the software. This process reduced the level of random noise on the signals allowing a more precise measurement of the peak to peak. This routine was repeated, typically, ten times to attain the required precision defined as the signal to noise ratio (**S/N**) of the system over these measurements.

### 3.2 System Description

The Oil In Water Monitor comprises three major sub-systems; the **Head Unit**, the **Control Unit** and the **User Interface PC** as shown in Figure 2 below.

- The **Head Unit** delivers the laser pulses via a sapphire window into the flow and contains the detection electronics for the Photo-acoustic response, as well as laser energy monitoring, temperature sensors and pre-amplifier. The pre-amplifier is required to be located near to the PZT (within 5cm), to reduce signal attenuation and maximise signal to noise ratio. The pre-amp amplifies the input signal by 62dB, which results in an output signal of around 40mV to 400mV. The pressure transducer is also mounted on the flange which is rated for working pressure up to 100 bar and process temperatures up to 100°C. The pressure transmitter returns a 4 – 20mA signal indicating the process pressure. There are two temperature sensors mounted in the head unit:
  - (I) Semiconductor temperature sensor potted in the Duplex Body using temperature conductive epoxy; the output from this is transmitted directly back to the control unit and indicates the process temperature.
  - (II) Semiconductor temperature sensor mounted on the Pre-Amplifier returns the temperature of the mounted electronics for condition monitoring.

The OIWM head unit was designed for installation onto a flanged interface. The flanged interface was at 90° to the direction of flow, which is required to be vertical upward. The mean flow direction passes across the head unit, with a clear flow path across the head unit optical window. Installation is in a vertical upward flow to promote an even distribution of oil droplets through the pipe cross-section at the head unit, and ensure a representative sample passes through the sensor measurement envelope. The mounting is by a 3 inch ANSI B31.3 900# flange to a weldolet or tee branch. Figure 3 shows the OIWM meter installed in the Environment and Resource Technology flow loop for test purposes.

- The **Control Unit** contains three main elements: the electronics and power supply stack, the laser drivers and terminal wiring and controls and co-ordinates laser firing, data acquisition, performs data reduction and outputs processed data to the display unit over a serial communication link using Modbus protocol. The laser driver assembly consists of two laser diode pulsers each driving a diode of different wavelength. The laser pulses are delivered to the head unit by fiber optic cables. The Head Unit is connected to the Control Unit via an armoured cable from the Pressure Transducer and armoured conduit through which the fiber optics and all other signals pass. The terminal wiring provides connections to the various pressure and temperature sensors and any signal conditioning required. Temperature sensors are located on the terminal wiring and in the laser driver for diagnostic purposes. The processing electronics is based on a card that can separate communications and interfaces from major data processing. The Control Unit operates independently, but to allow monitoring of the data during logging, some of the data is transferred to the User Interface PC via a serial link. The control unit is designed for use in a non-hazardous area.
- The User Interface PC is a standard PC, with custom windows software which displays data from the Control Unit and indicates the system status using a series of green or red boxes.

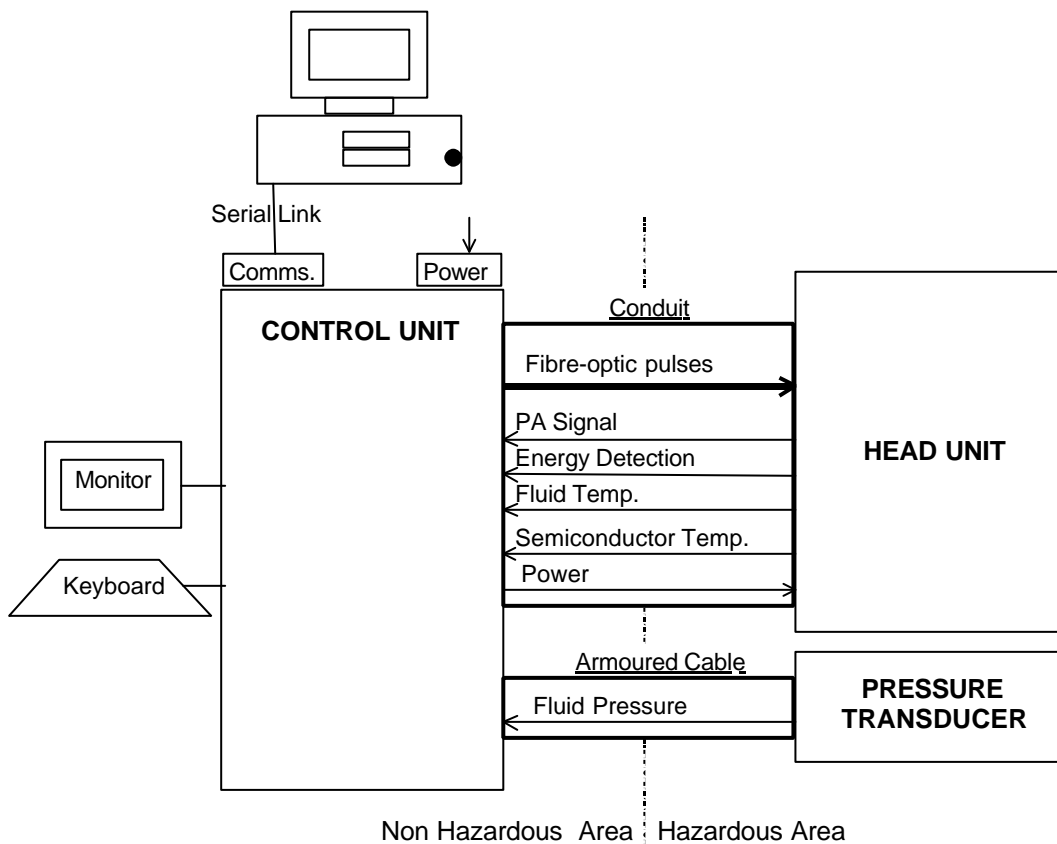
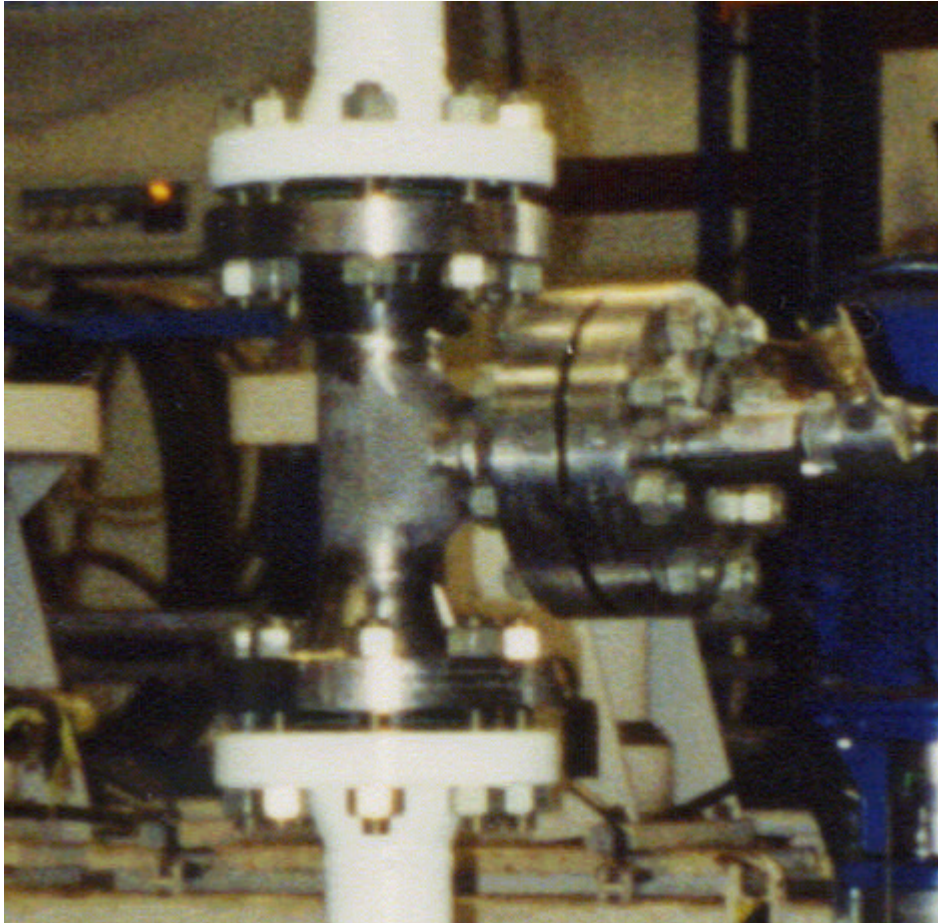


Figure 2 - Oil In Water Monitor System Block Diagram



**Figure 3 - Oil In Water Monitor Site Installation**

#### **4 TESTS AND RESULTS**

To investigate the suitability of the prototype instrumentation for monitoring crude oil concentrations in produced water, preliminary field testing of the instrumentation was undertaken at the Orkney Water Technology Center (part of Environment and resource Technology, Ltd), Flotta, Stromness, Orkney Islands, UK, part of the COSWASS program, from 11<sup>th</sup> of March till end of August 2000. This facility is highly regarded and supported by the offshore oil industry and carries out testing of offshore equipment, including control and monitoring Instrumentation. Facilities include the simulation of produced water samples, which can be employed to test sensor systems in a more controlled environment.

To achieve reliable and repeatable conditions a detailed test matrix was agreed and adhered to throughout the test program. To evaluate the potential of the prototype instrumentation for the measurement of crude oil concentrations in water, the trend of the photo-acoustic response of oil concentrations was investigated over a range of aqueous conditions.

Two different types of crude oils have been used (Flotta and Foinaven crudes) both typical North Sea Oils. The same sequence of tests was carried out using each oil. The oil concentrations were between 20ppm to 2000ppm. See Appendix for full test matrix.

Reference Measurements at ERT were carried out using InfraRed Analysis of samples and from the set point dosing pumps, both with an accuracy of  $\pm 10\%$ .

#### 4.1 Linear Response (Pa Versus Oil Concentration)

A linear trend of the magnitude of the photo-acoustic signal versus oil concentration was achieved for 20 to 2000ppm with both types of crudes. Figure 4a shows this trend for the Flotta crude. It can be seen here that an increase of  $20\mu\text{V}/\mu\text{J}$  for the Flotta crude in the photo-acoustic response of the system has been measured from the lowest to the highest concentrations. With a sensitivity of less than  $0.1\mu\text{V}/\mu\text{J}$  the OIWM system should be potentially capable of measuring changes of 10ppm.

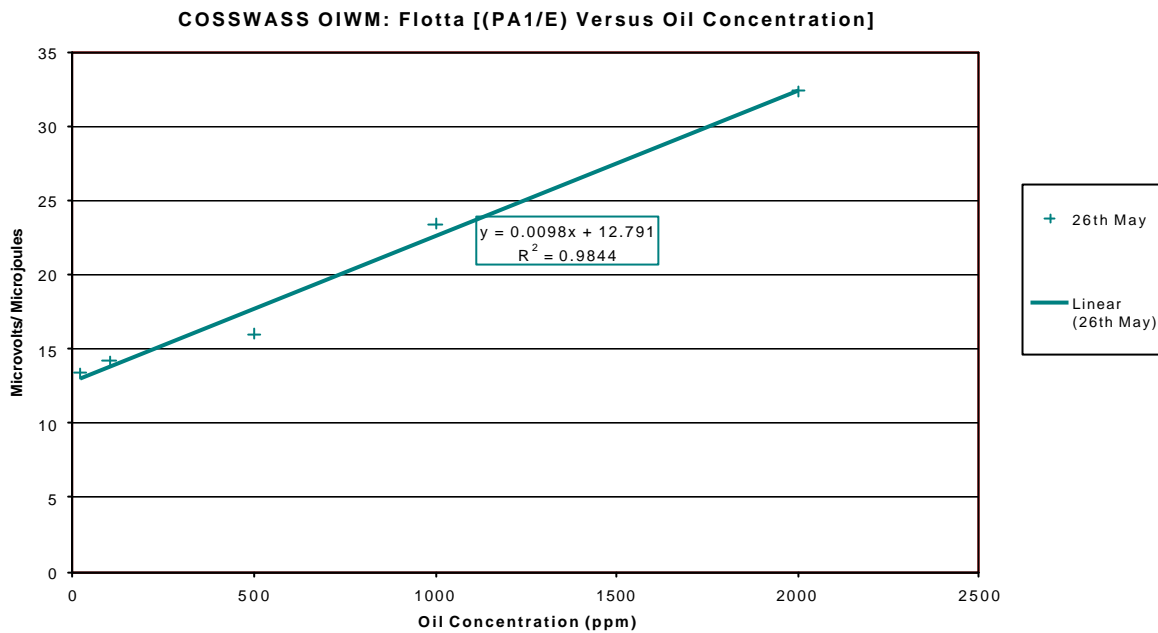


Figure 4a - Linear PA response using Flota crude

The OIWM also displayed good linearity of response with Foinaven crude (Figure 4b), at a similar response level. Sensitivity will be similar for both oils.

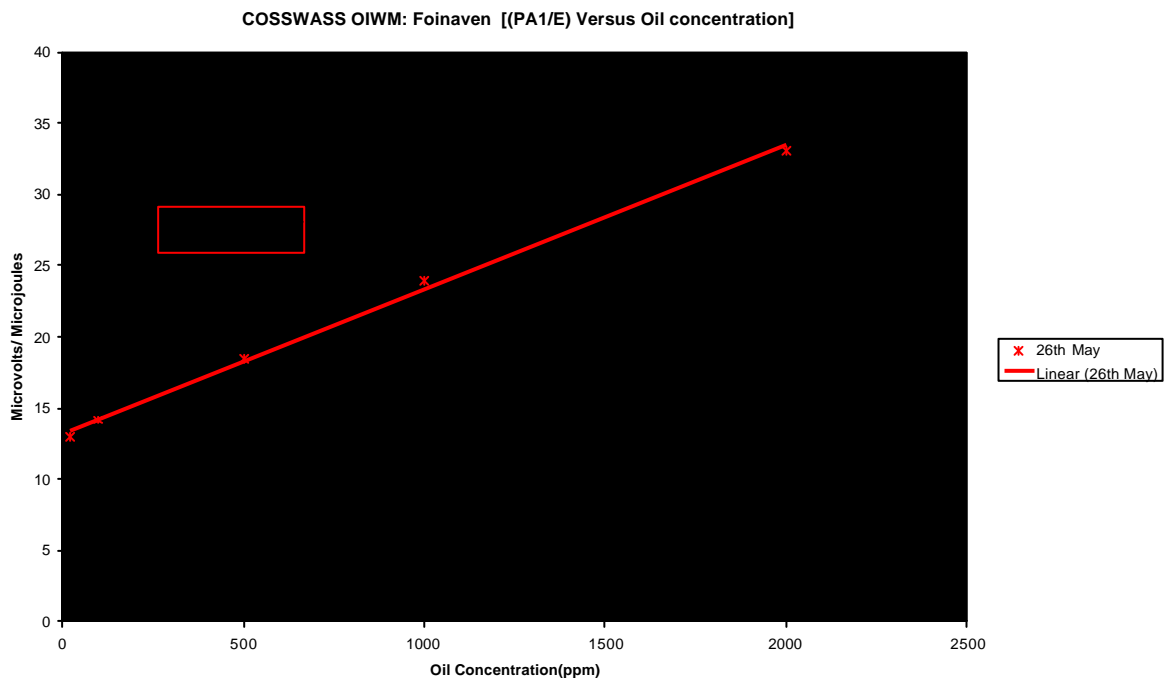
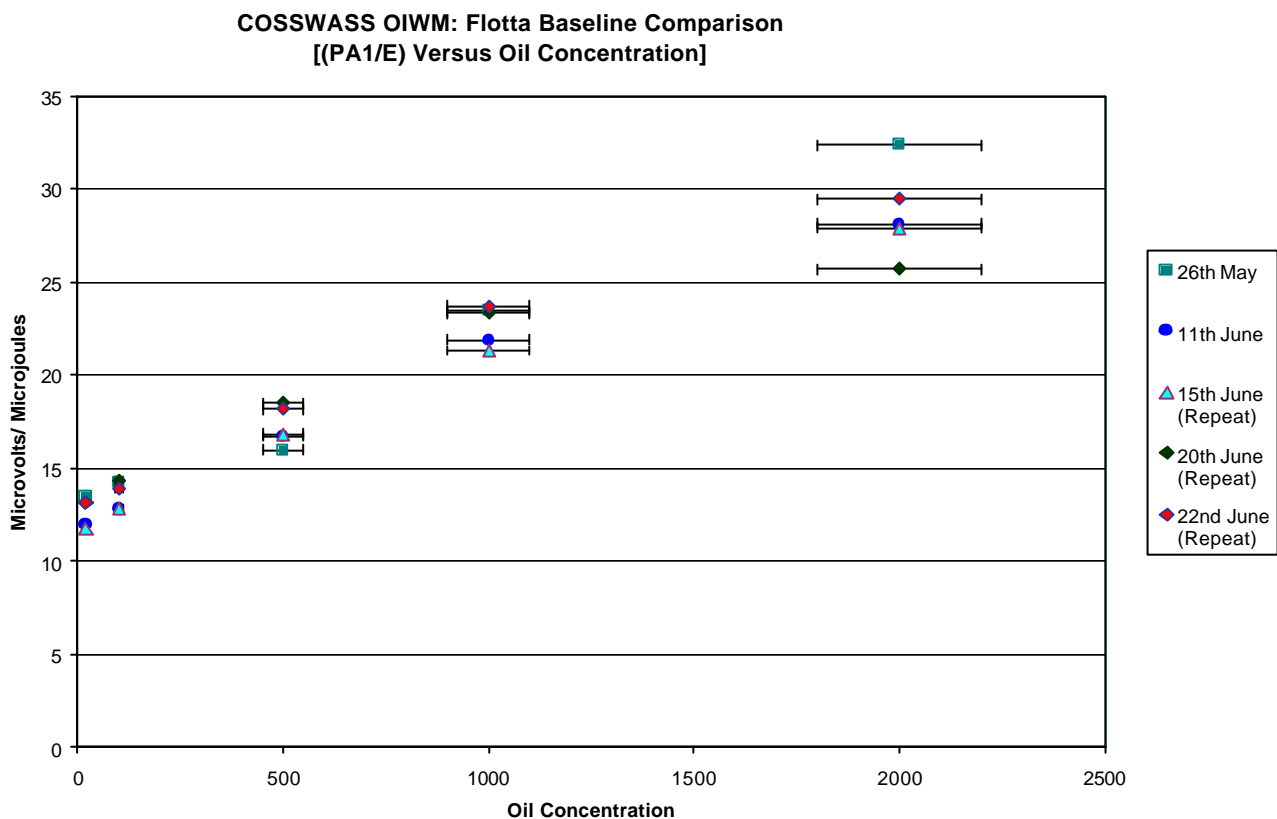


Figure 4b - Linear PA response using Foinaven crude

## 4.2 Reproducibility Response

Another important characteristic of the system that was closely monitored was the reproducibility of the measurements. At the beginning and/or end of a set of tests, readings were repeated at a standard set of conditions (refer to here as **Baseline**) at a temperature of 45°C, pressure 10bar, flow velocity of 4msec<sup>-1</sup>, at all oil concentrations (20,100,500, 1000,2000ppm). These measurements were repeated at regular time intervals and in the same order. The results of some of these are plotted in Figure 5 below. It is noticeable how repeatable the normalised Photo-acoustic response of the system is. The slight variations seen are due to small temperature fluctuations in the head of the unit. Error bars refer to the uncertainty of the ERT reference measurements.



**Figure 5 - Reproducibility Response of the OIWM with the Flotta Crude**

## 4.3 Fouling Of The Sapphire Window

Following collation of early test data it was noted that the response of the OIWM was changing with time, giving changes in the gradient of the response. On removal of the head for investigation it was noted that the optical window was significantly fouled. The head was cleaned and returned to the line and the photo-acoustic response of the monitor was also returned to that originally observed.

Although fouling of the optical window was observed over a period of time, it should be noted that the overall response of the monitor remained linear for all the oil concentrations and for both crudes. The fouling was attributed to the various additives added to the water for the tests as well as the oil and dirt/corrosion products from the flow loop. It is believed that an oil film of a few microns was formed in front of the sapphire window; the thickness of this film will vary depending on the test i.e. whether there were demulsifiers and/or corrosion inhibitors as

well as oil injected in the loop. The effect on the measured signal can be seen in Figure 6. The gradient of the response in the fouled head is reduced and the intercept is increased. Linearity of the response is unaffected by the fouling. The effect is typical for all degrees of fouling.

In practice although the laser pulse energy is absorbed in both the fouling and the oil in water, the sum of these two responses gives a perfect linear response to the oil concentration over the entire range, even with severe fouling.

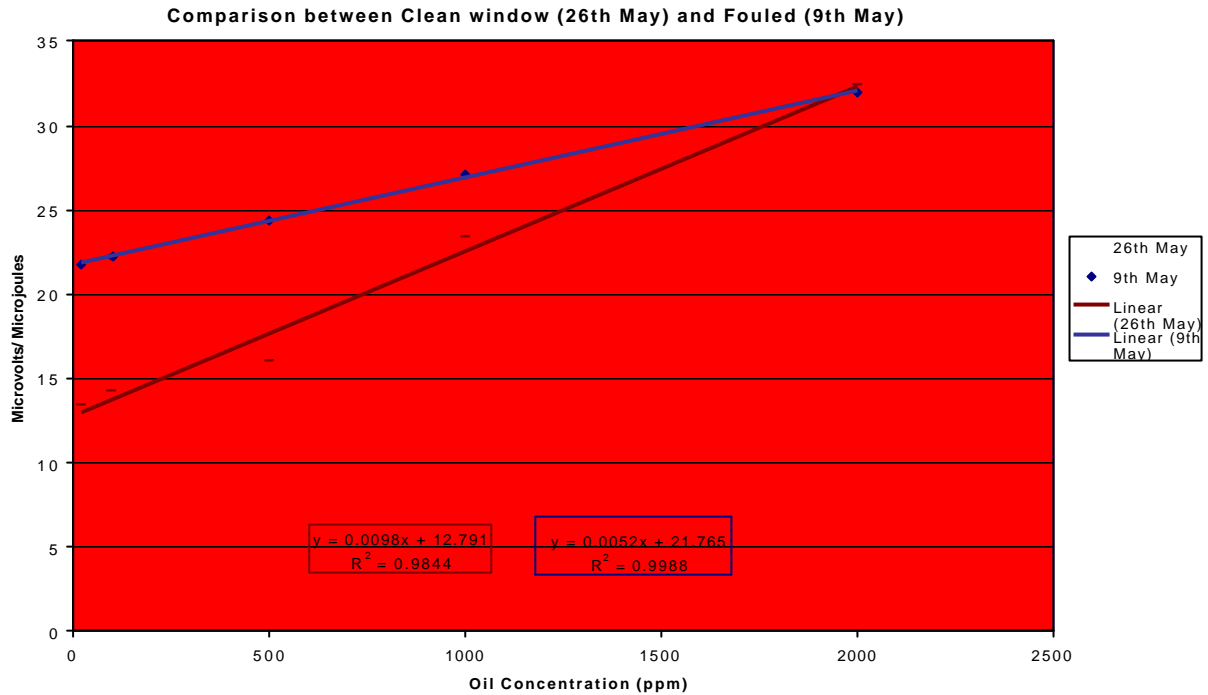


Figure 6 - Comparisons between clean and fouled heads using Flotta crude

#### 4.4 Response To Different Types Of Crude Oils

The linear response of the OIWM was maintained for both different crude oil and concentrations Flotta and Foinaven as shown in Figure 7 below. The photo-acoustic response is similar; the variances are mainly due to the different characteristic physical properties of the two types of crude. The error bars indicated the uncertainty of the measurements due to the flow loop reference system.



COSWASS OIWM: Foinaven and Flotta comparison  
 [(PA1/E) Versus Oil concentration]

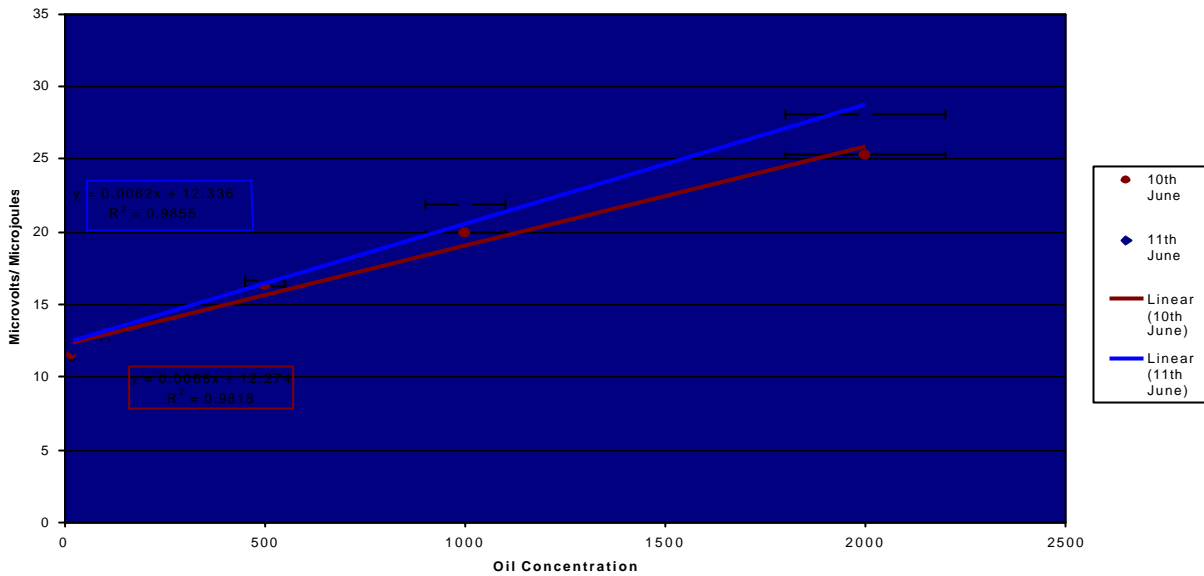


Figure 7 - Comparisons of PA response for both Crude Oils

#### 4.5 Response To Injection Of Chemicals

The tests with the injection of various chemicals encountered in the offshore production such as corrosion and scale inhibitor, showed that the sensitivity of the photo-acoustic trend with oil concentration was not changed due to their presence, but although a shift in the background response from water was observed. Figure 8 below shows some of these trends with the Foinaven oil; similar responses were obtained also with the Flotta crude.

Chemical Comparison: Foinaven Crude  
 (PA1/E Vs Oil Concentration)

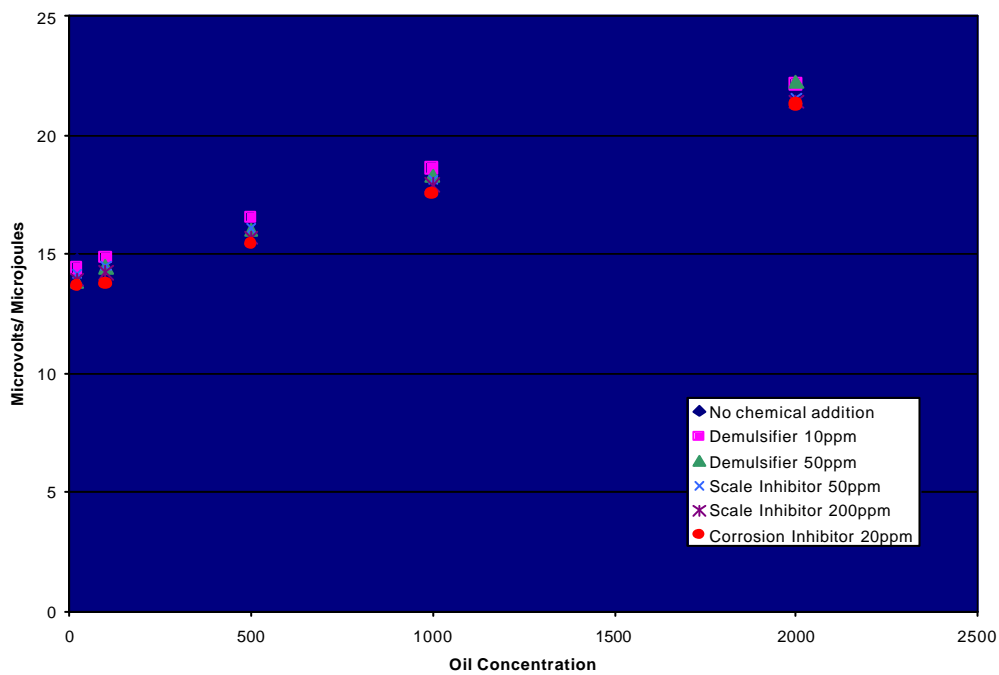


Figure 8 - Comparisons with injection of various chemicals using Flotta crude

#### 4.6 Response To Different Size Oil Droplets

The photo-acoustic response of the OIWM was also found to be independent of the oil droplet size over the mean distribution range of 20-50 $\mu\text{m}$ , (the range typically found offshore) further strengthening the suitability of pulsed photo-acoustic instrumentation for this application.

A drop in the normalised PA signal was noted for the case of droplets of 100 $\mu\text{m}$ ; this was attributed to the greater scattering caused to the photo-acoustic pulses from the large size oil droplets. Figure 9 shows some of these responses when Flotta oil is used, where signal amplitude is reduced but sensitivity is retained. Similar behaviour is noted with the Foinaven crude.

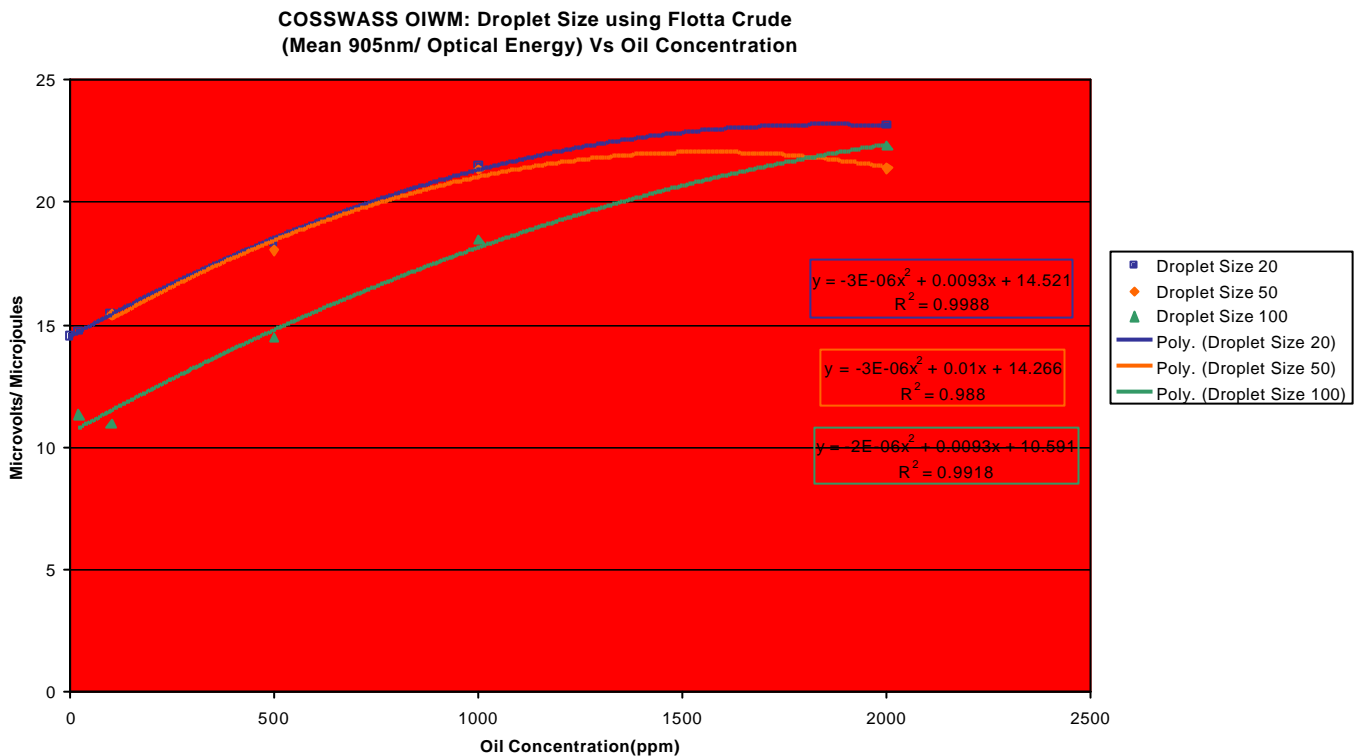
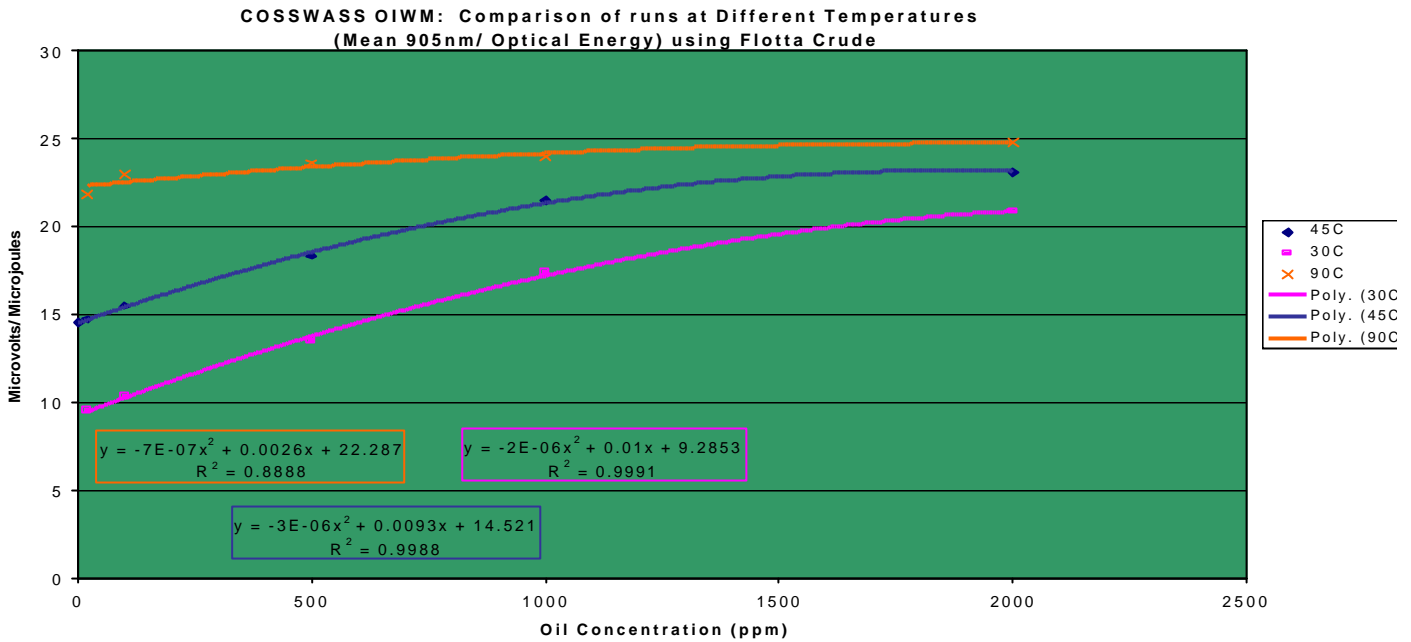


Figure 9 - Runs at different droplet sizes with Flotta crude

#### 4.7 Response To Varying Process Temperature

The photo-acoustic response of the OIWM was also investigated with varying oil concentrations and varying process temperatures. Typical plots obtained are shown in the Figure 10 below for the Flotta crude. Similar responses were registered for the Foinaven oil. The dependency of the Photo-acoustic pulses to a number of physical parameters has been described earlier. Hence the characteristic behaviour of the system for the three different temperatures 30°C, 45°C and 90°C plotted below.

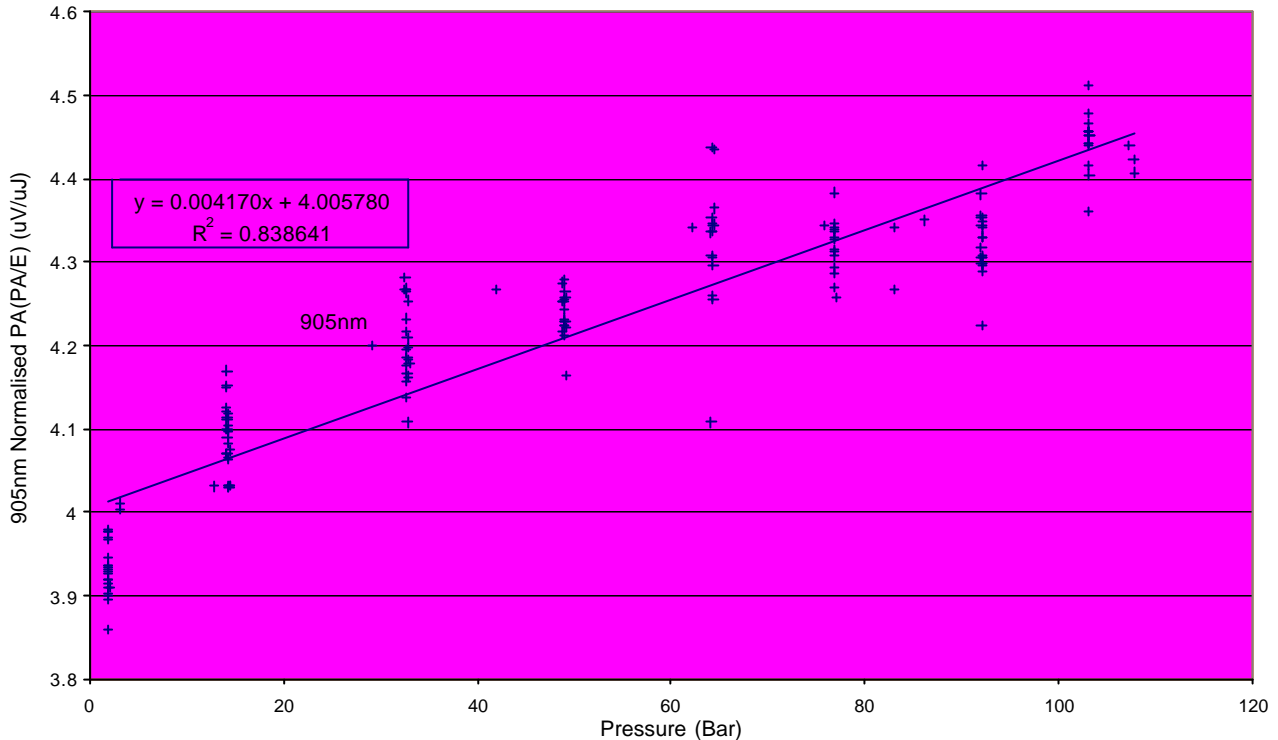


**Figure 10: Runs at different process temperatures with Flotta crude**

Similar responses were observed with the same monitor during static tests in the laboratory prior to the site installation in the ERT Flow Loop.

#### 4.8 Response To Varying Process Pressure

Previously during Phase 1 of the COSSWASS program a series of tests were carried out over a range of crude oil concentrations in water at a variety of pressures from 100 bar to 350 bar. At this stage Phase 2, tests were carried out for static pressures of 0 to 100 bar. The data from the flow loop tests for the varying pressures with a range of oil concentrations have not been analysed yet; however, a similar response is expected. Figure 11 displays the raw data (not averaged) of the photo-acoustic signals plotted against the pressure range for a static system i.e. in the laboratory. An increase of  $\sim 0.5\mu\text{V}/\mu\text{J}$  is measured when the pressure increases from atmospheric to 101 bar a. These results show the dependency of the signal to the physical parameters that characterise the monitor response as described earlier. These are also in agreement with the theoretically predicted behaviour of the system and with previous observations.



**Figure 11 - Runs at different process pressures**

## 5 DISCUSSION

During Phase 2 of the COSWSASS program a formidable range of data has been collected from 1123 individual measurements.

The suitability of this instrument to monitor oil concentrations in water from 20 to 2000ppm has successfully been demonstrated. The linear response of the photo-acoustic pulses was maintained for both crude oils (Flotta and Foinaven). Differences in their physical properties can be readily accounted for in calibration.

Further measurements found that the sensitivity of the photo-acoustic trend with oil concentration was not changed by the presence of chemicals commonly encountered in offshore production

The photo-acoustic response was also found to be unaffected by the oil droplet size for the range of 10-50  $\mu\text{m}$ . The range typically found in the produced water systems is  $\sim 30 \mu\text{m}$ .

Fouling of the optical element did occur to different degrees throughout the period of the trials. The thickness of the film did vary depending on the additives present in the loop at the time of measurement. The linear response of the monitor was maintained with a fouled head.

The normalised PA signal with a fouled window did change (increased intercept and reduced gradient). This is expected to be corrected by enhanced signal analysis. The sensor head was cleaned after 3 months of testing and subsequently was cleaned at regular intervals to generate data for a "clean" baseline characterisation to which the "fouled" data could be compared. Reproducibility in both clean and fouled conditions was within the expected range.

The behaviour of the system was also investigated for the same range oil concentrations at a variety of temperatures, from 15°C to 90°C and pressures from 0 to 100 bar respectively. The behaviour noted was due to the changes in the physical parameters upon which the pulsed photo-acoustic signals are dependent, and followed trends expected from theory.

Reproducibility and robustness are some of the necessary qualities of any system/instrument suitable for offshore installation. No failures were encountered during this “hands-off” trial of the OIWM. The only support activity was to clean the instrument head regularly. This involved manual handling of the instrument and the robustness of the instrument was further demonstrated by the lack of hardware problems caused by handling.

#### **ACKNOWLEDGEMENTS**

The authors would like to express their gratitude for the funding and support of the COSWASS JIP and its members in this test program. Also, we would like to thank ERT for carrying out the numerous tests and data collection/management.

**APPENDIX**

**TEST MATRIX**

	Oil Conc (ppm)	Chemicals (ppm)	Oil Droplet Size (?m)	Velocity (m/s)	Flowrate (m <sup>3</sup> /h)	Pressure (Bar)	Temperat. (°C)	Gas (%v/v)	Solids (ppm)	Noise (Hz)	Foulin g	Salinity (g/l)	Calibration (2 oils)	No.of Point
1	20, 100, 500, 1000, 2000		50 (max)	4	65.7	10	45					33	Flotta, Foinaven	10
2	20, 100, 500, 1000, 2000	De-mulsifier (10, 50 ppm), Scale inhibitor (50, 200 ppm), Corrosion inhibitor (20, 200 ppm)	50 (max)	4	65.7	10	45					33	Flotta, Foinaven	60
3	20, 100, 500, 1000, 2000		20, 50, 100 (mean)	4	65.7	10	45					33	Flotta, Foinaven	30
4	20, 100, 500, 1000, 2000		50 (max)	1.5,2.5, 5	24.6, 41	10	45					33	Flotta, Foinaven	30
5	20, 100, 500, 1000, 2000		50 (max)	4	65.7	5,40, 80,100	45					33	Flotta, Foinaven	40
6	20, 100, 500, 1000, 2000		50 (max)	4	65.7	10	15, 30, 45, 90					33	Flotta, Foinaven	30
7	20, 100, 500, 1000, 2000		50 (max)	4	65.7	10	45	1, 2				33	Flotta, Foinaven	20
8	20, 100, 500, 1000, 2000		50 (max)	4	65.7	10	45		0, 25, 100, 300			33	Flotta, Foinaven	40
9	20, 100, 500, 1000, 2000		50 (max)	4	65.7	10	45			Valve, 2 settings		33	Flotta, Foinaven	
10	20, 100, 500, 1000, 2000		50 (max)	4	65.7	10	45				Scale	33	Flotta, Foinaven	1 week
11	20, 100, 500, 1000, 2000		50 (max)	4	65.7	10	45					0, 66, 99	Flotta, Foinaven	30

## References

[1] Paper presented at the North Sea Flow Measurement Workshop, a workshop arranged by NFOGM & TUV-NEL

Note that this reference was not part of the original paper, but has been added subsequently to make the paper searchable in Google Scholar.