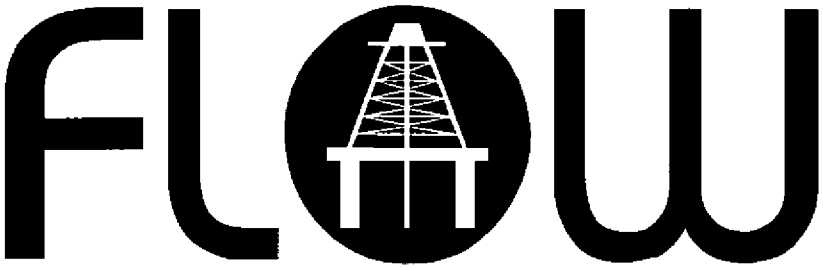
North Sea



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MONITORING OF DISSOLVED AND DISPERSED HYDROCARBONS IN PRODUCED WATER BY PHOTOACOUSTIC SPECTROSCOPY

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1 INTRODUCTION

Photoacoustic spectroscopy is a long established technique which has been revitalised by the availability of new optoelectronic components from the telecommunications industry. The combination of near infrared diode laser sources, optical fibres and fibre optic components all contribute to continued development of a new generation of analytical instruments for applications in both the environmental and health care areas. In addition, when the advantages of the photoacoustic technique are allied to state of the art electronic devices and advanced computing modules an innovative instrument becomes feasible which overcomes many of the limitations of current techniques.

Photoacoustic generation is complex interaction involving physical and optical parameters which include the specific heat capacity c_p, the thermal expansion coefficient β and the velocity of sound v so that the magnitude of the photoacoustic signal can be expressed as

$$V_{pa} = k.\frac{E\ \alpha\ \beta\ v^{\frac{1}{2}}}{c_p}$$

where k is a constant of the instrument, E is the laser pulse energy and α is the optical absorption. A typical photoacoustic signal is shown in Figure 1 where the time interval between the start of the trace and photoacoustic signal at 4μS is the acoustic transit time from the optical beam to the acoustic detector and may be used to measure the velocity of sound in the liquid.

In general the peak to peak amplitude of the photoacoustic signal, **PA**, at a selected wavelength is used to measure the concentration of a particular analyte and to compensate for energy fluctuations, the amplitude is divided by. **E**, the energy of the optical pulse. Thus **PA/E** is the normalised photoacoustic amplitude which is used throughout our results.

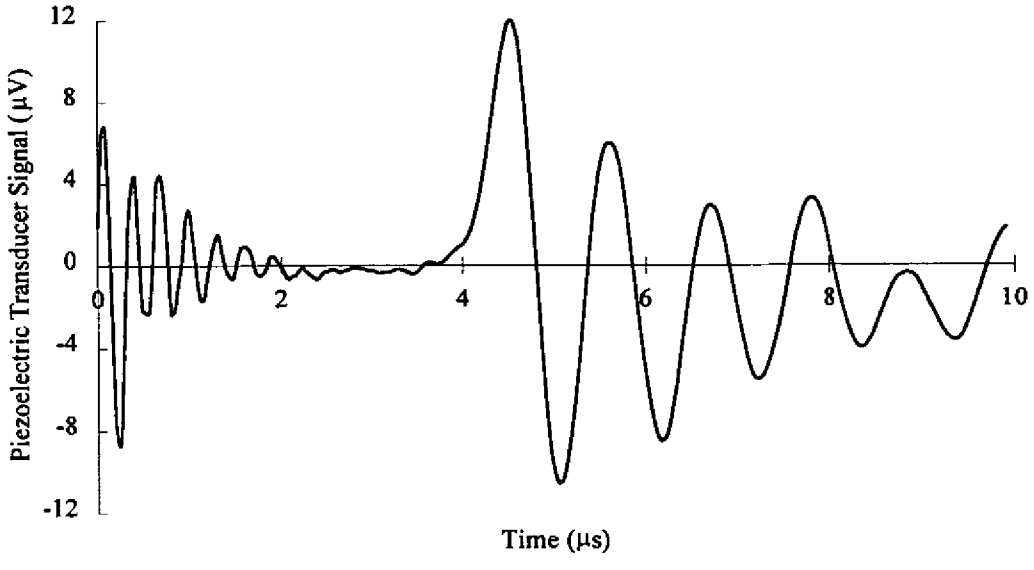

Figure 1 - Showing pick up at the start of the trace followed by the photoacoustic signal

The combination of physical parameters for water do not favour a strong photoacoustic response whereas those for many hydrocarbons yield a favourable set of properties and as a consequence the near infrared (NIR) spectrum of is comparatively weak and the spectral response for hydrocarbons is relatively strong.

The basic principles of sensing oil in water have been established both in the laboratory and through preliminary testing at the Orkney Water Test Centre and a typical response to Flotta crude is shown in Figure 2. These tests also served to show, within the limits of the tests, that the photoacoustic response was not affected by droplet size or flow velocity. Based on the success of the laboratory sensor, the design requirements for a dedicated instrument for offshore use has been achieved.

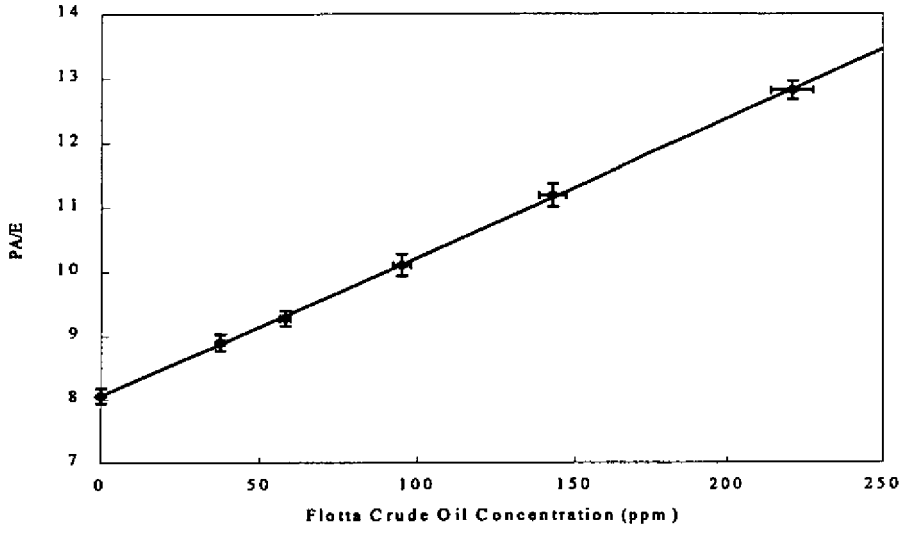

Figure 2 - The photoacoustic sensor response to changes in oil concentration in the test facility at the Orkney Water Technology Centre (ERT)

2 EXPERIMENTAL RESULTS

In the project proposal, some twelve key areas were identified to map out the progress of this project and at this halfway point, seven of these areas have been investigated in detail and in the following section, the experimental results will be presented for a laboratory photoacoustic sensor which was utilised to explore the use of photoacoustics in offshore applications, the results of which were applied during the design and development of a dedicated instrument for this project. The preliminary results of the hydrocyclone test rig development will also be discussed.

2.1 Performance in the Presence of Chemical Additives

In an offshore environment , the sensor will be required to monitor the level of oil concentrations in the presence of complex additives such as dispersants and corrosion inhibitors. We have conducted initial studies using additives at concentrations up to 1000 ppm and have found that the sensitivity to oil detection is unimpaired but there are changes in the baseline response. As we are using a dual wavelength system, this aspect will be included in the calibration algorithm.

Figure 3 shows the basic response of Flotta crude in salt water. It should be noted that the sensitivity to oil is characterised by the slope of the line which in this case is 0.011. The base line corresponds to the response in the absence of oil and in this case has a value of 17.2. When 1000 ppm of Methanol was added to the sample the response was as shown in Figure 4.

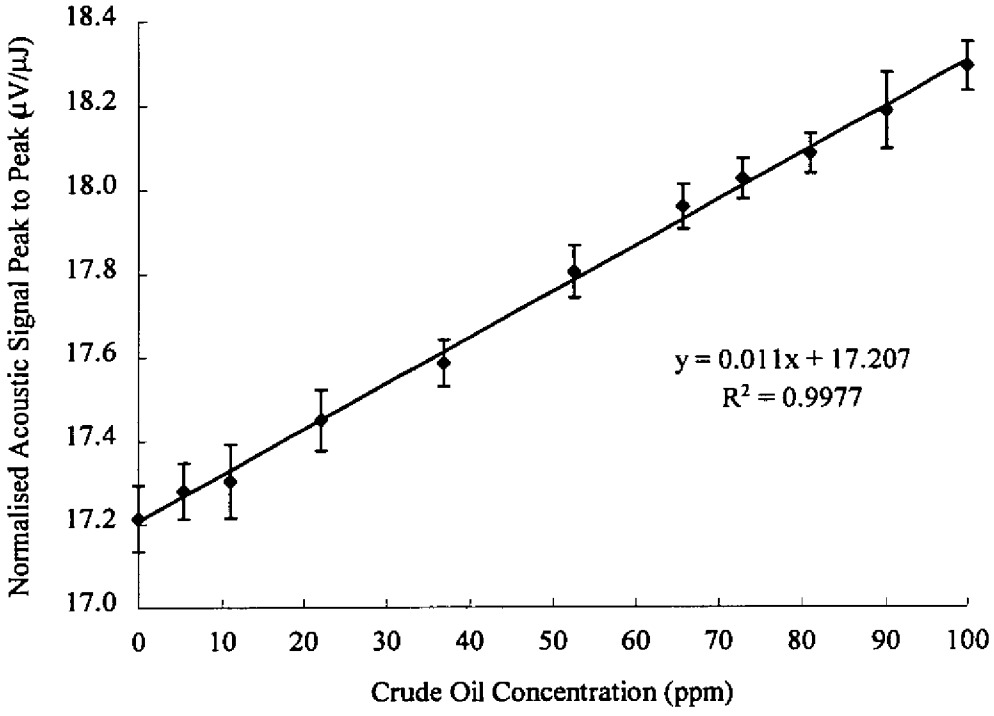

Figure 3 - Showing the response to changes in Flotta crude concentrations in salt water

It will be seen that the slope of the response remains approximately as before but the intercept at 0 ppm is now at 19.5. In the same way, when 1000 ppm of corrosion inhibitor is added, the sensitivity remains constant but the base line changes as shown in Figure 5.

The initial conclusion from these experiments is that the sensitivity of the photoacoustic sensor to oil concentrations is not affected by the presence of additives but baseline compensation will be required in the data analysis. For this reason , two wavelengths are used in the practical instrument: One for baseline compensation and the other for analyte measurement.

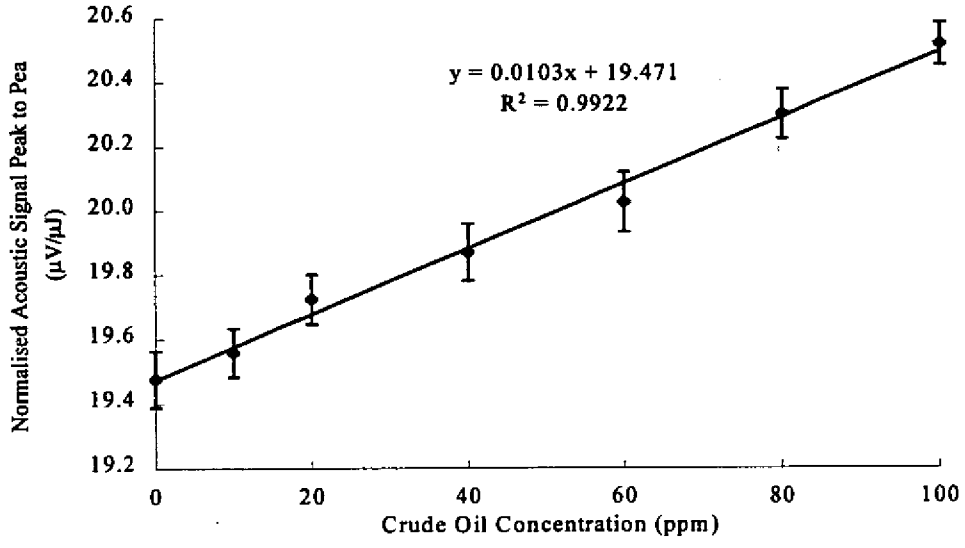

Figure 4 - Low crude oil concentration photoacoustic response in salt water with 1000ppm of methanol present

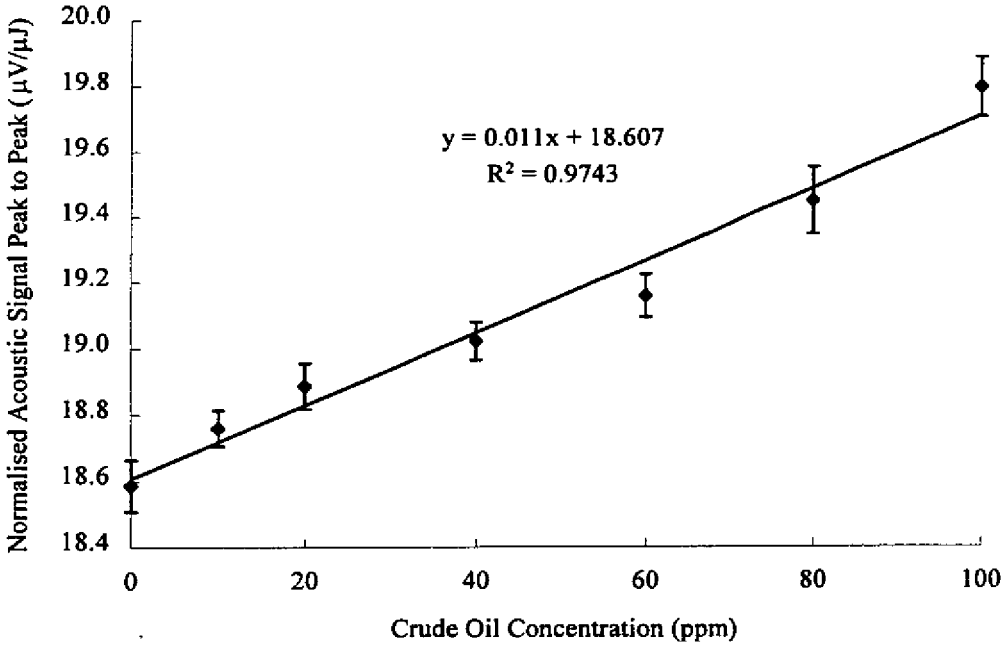

Figure 5 - Low crude oil concentration photoacoustic response in salt water with 1000 ppm of corrosion inhibitor present.

2.2 Performance at High Pressure

The operation of the photoacoustic sensor in hydrocyclone applications requires a system which will operate at pressure. When a high pressure cell was made available, investigation of the photoacoustic response at high pressure was undertaken. The high pressure values of the key physical parameters for water are available from tables in textbooks and scientific references. From this data and by substitution in the basic photoacoustic equation, the predicted photoacoustic response over a pressure range was calculated and is shown in the pressure range 1 to 350 bar as the straight line in Figure 6. A set of data points from photoacoustic measurements is also shown and there is clearly an excellent correlation between predicted and actual response. The continued functionality at high pressure is an interesting pointer to the possibility of subsea applications.

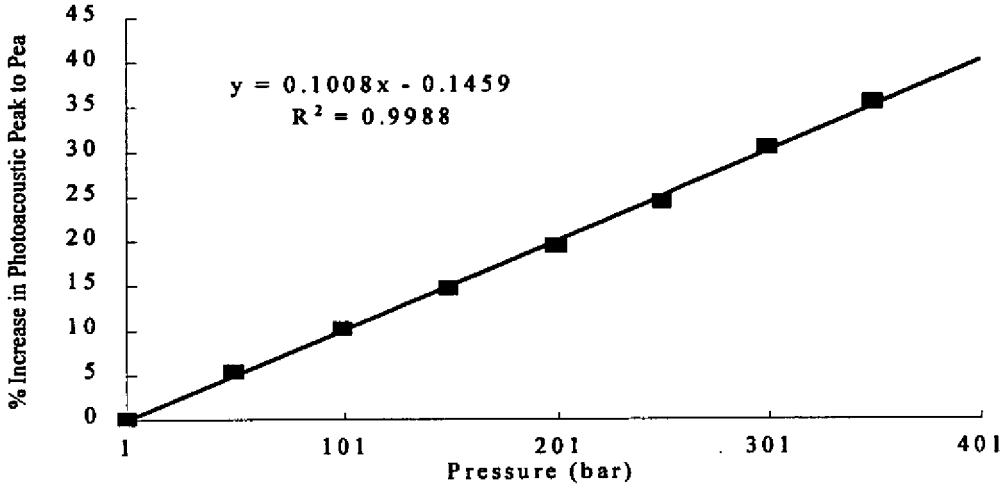

Figure 6 - Comparison of experimental results (symbols) and theoretical prediction (line) of the effect of pressure on the photoacoustic response from water

2.3 Performance with Different Crude Oils

A key factor in the calibration of the photoacoustic sensor is knowledge of the spectral response to different crude oils. Clearly if there was a dramatic and unpredictable difference in response it would create formidable calibration problems. To explore this aspect, samples of seven different crude oils were investigated and the resultant spectra are shown in Figure 7 below.

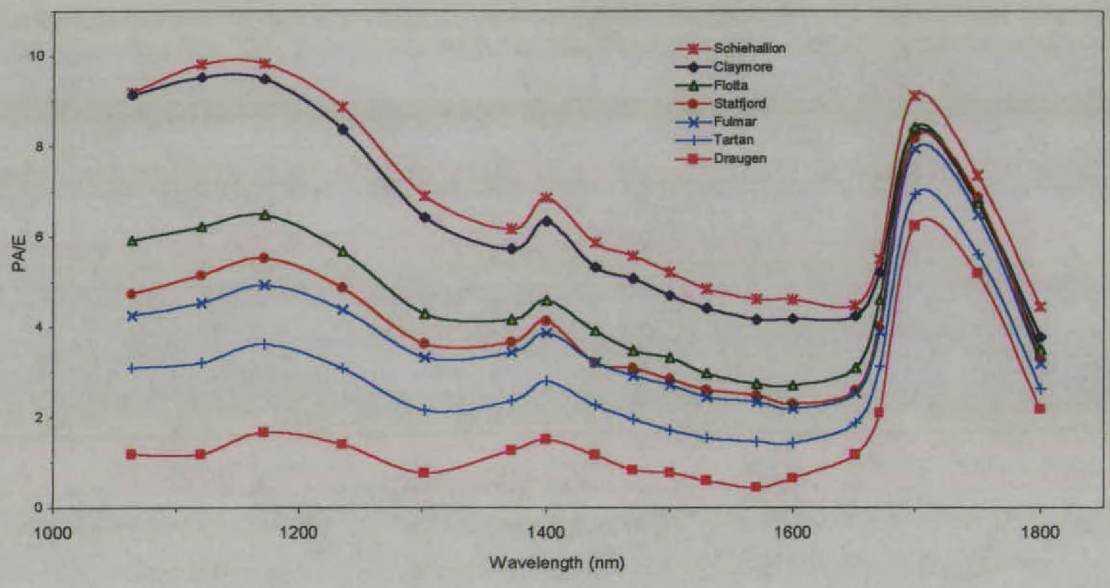

Figure 7 - Photoacoustic Spectra of various crude oils

It will be seen from these results that all the oils show the same general features of spectral peaks which are common to most hydrocarbons and a background response which is attributed to asphaltene products. Clearly with multi-reservoir systems, the changes in oil type would need to be included in the calibration process but it seems at this stage that different crude oils have substantially the same spectroscopic response against a background of broad band absorption from complex asphaltene compounds.

2.4 Temperature and Salinity Tests

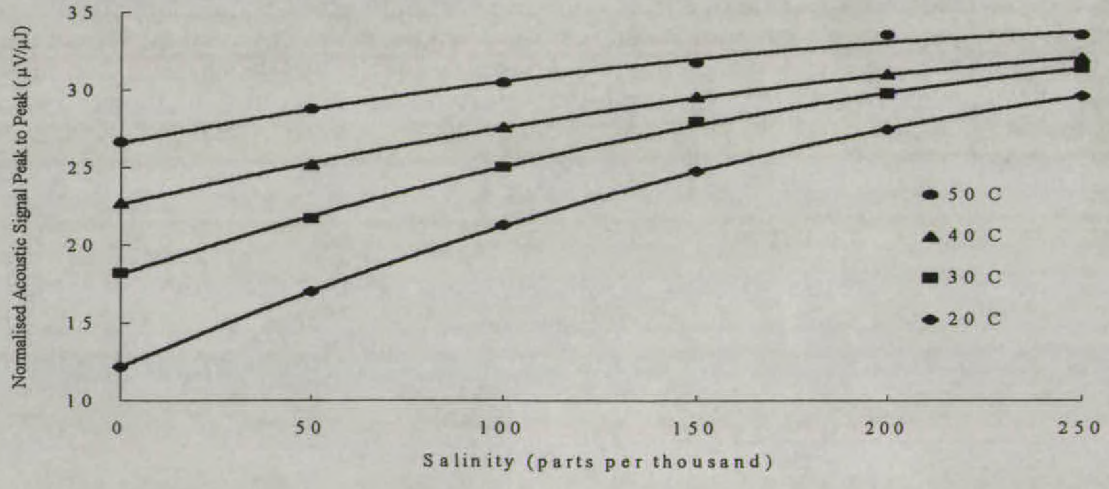

Figure 8 - Photoacoustic response from water with various salinities and temperatures

In the current sensor head there is an accurate temperature probe and there is a simple linear relationship between salinity and the velocity of sound in salt water. The velocity of sound in the sample may be measured from the delay time between the optical pulse and the onset of the photoacoustic signal. These measurements are an integral part of the calibration algorithm.

2.5 Response of Crude Oil Components

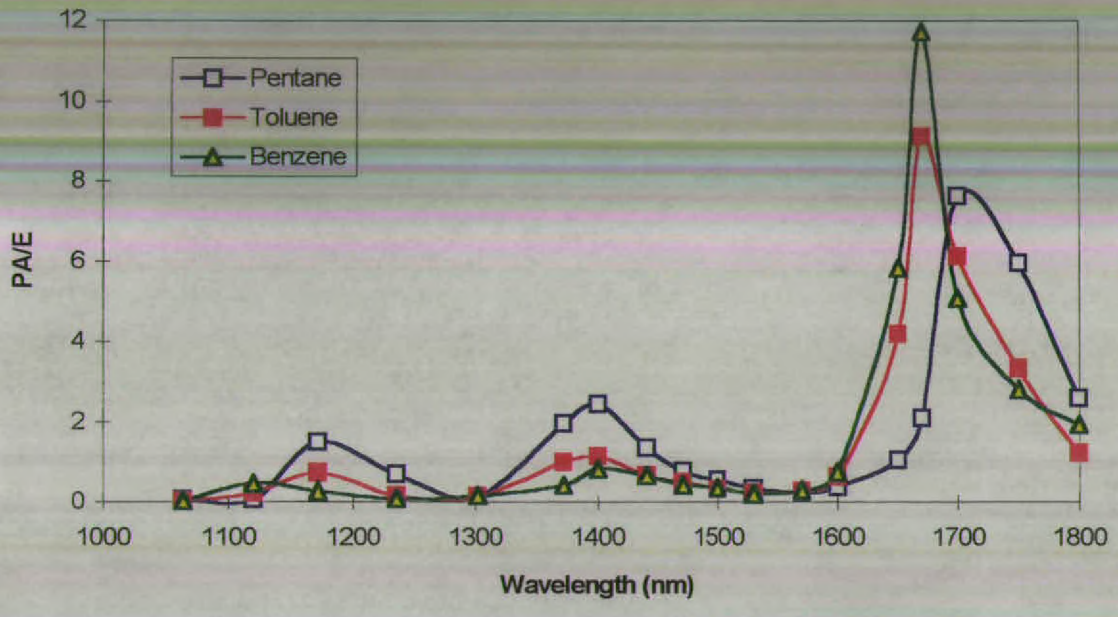

Figure 9 - Photoacoustic spectra of Pentane, Toluene and Benzene

Raw crude oils are complex liquids which comprise many components both volatile and non volatile. The spectra of Pentane, Toluene and Benzene are shown in Figure 9 below and have the characteristic spectra of light hydrocarbons. It is interesting to note in Figure 9 that the differences in peak positions around 1650 to 1700 nm is as predicted from conventional spectroscopy of these materials and suggests that an analytical photoacoustic instrument may be a possibility at a later date.

To investigate the role of the different components of a typical crude in creating the overall photoacoustic response a sample of Statoil crude was fractionated into four components and the photoacoustic spectrum of each component was recorded as shown in Figure 10. It will be seen that the lighter fractions, for example F1, have spectrum which are similar to those shown in Figure 9 whereas the heavier fractions such as F4 have a comparatively smooth and featureless response which increases at the shorter wavelengths in keeping with the background response expected from the heavier components.

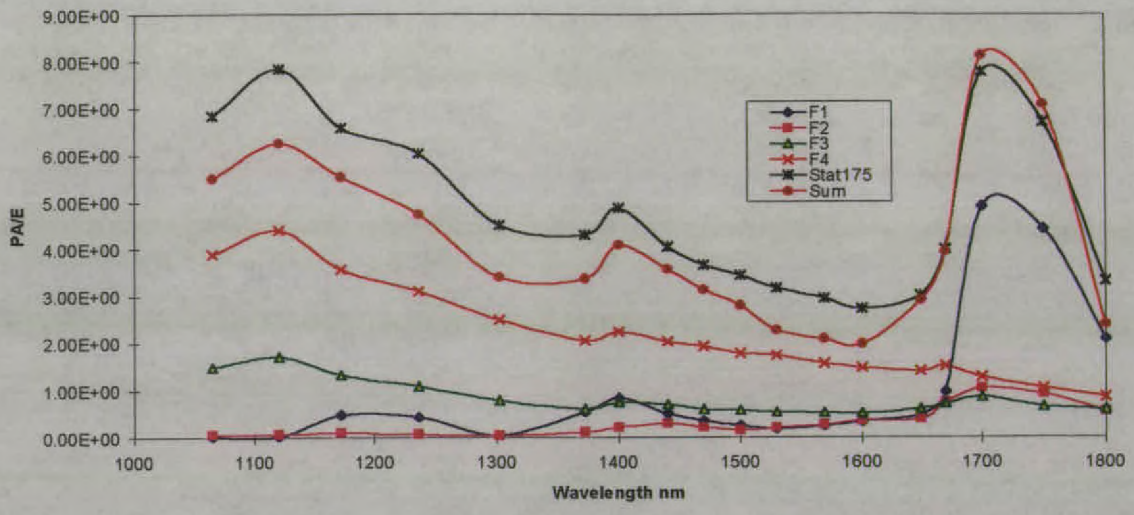

Figure 10 - Photoacoustic Spectra of crude oil fractions

2.6 Response at High Oil Concentrations

The original specification for this type of photoacoustic sensor was for the topside discharge of produced water with oil concentrations in the 10 to 100 ppm range. To establish the suitability of the photoacoustic sensor for monitoring the input side of a hydrocyclone, measurements were made at higher oil concentrations. Figure 11 shows the photoacoustic response in the range 0 to 8000 ppm of crude oil and it can be seen that the response is completely linear up to the highest concentrations.

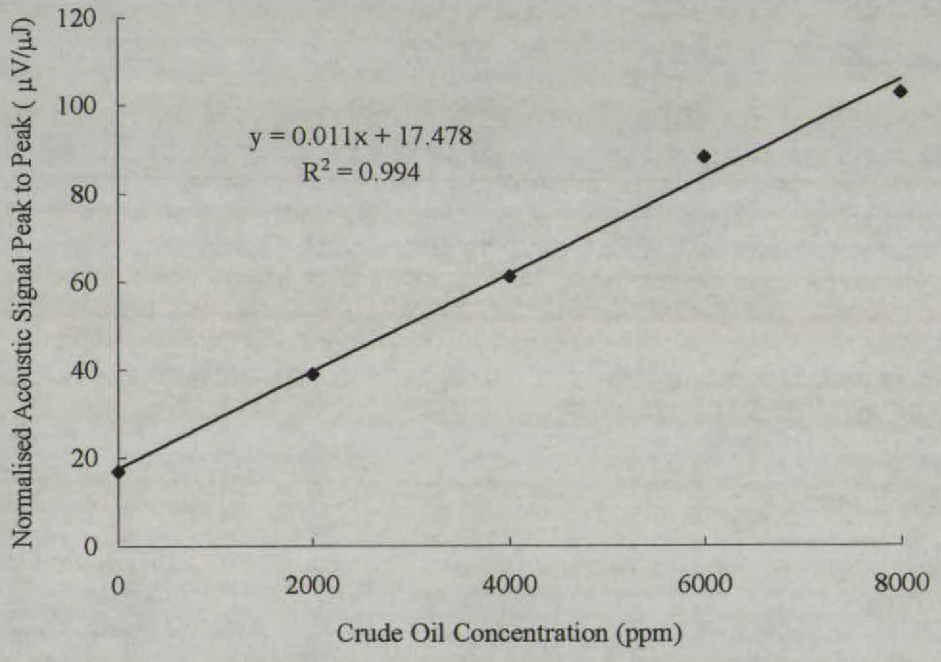

Figure 11 - High concentration measurements on Flotta Crude oil in water with laboratory system

At the higher concentrations, it was difficult to maintain the oil concentrations in emulsion for a reasonable time interval and it was decided to explore percentage oil concentrations in carbon tetrachloride. This liquid does not have spectral features in the relevant spectral region and is an ideal solvent for this application. The results of these experiments are summarised in Figure 12

which has measurements in the 0 to 20% oil concentration range. The response is fairly linear up to 10% and there is a roll off in sensitivity up to 20%. As mentioned previously, the detector head was designed for optimum response at lower oil concentrations and it should be possible to optimise the response in a similar way for higher concentrations.

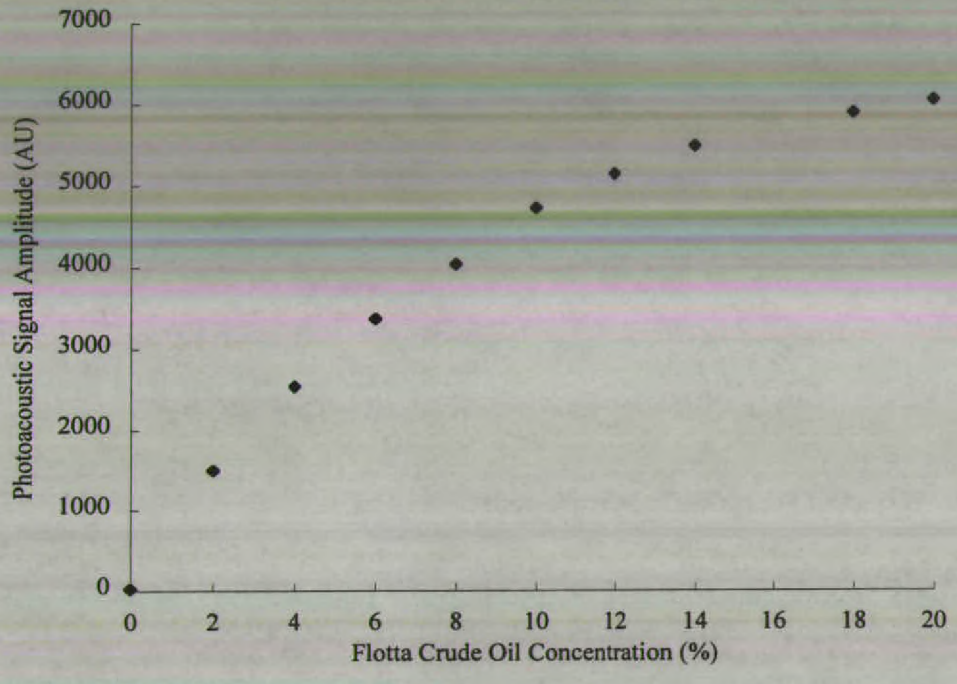

Figure 12 - Photoacoustic response for crude oil in carbon tetrachloride

2.7 Design Considerations

The sensor head consists of a 38 mm diameter stainless steel tube with the photoacoustic sensor system at one end and a 5 m umbilical to the control system at the outer end. The tube can be fitted into the test system either by a flange or by compression fittings. The photoacoustic sensor system consists of an optical system which directs a focussed laser beam through a sapphire window into the measurement region where the photoacoustic response is generated and detected by a curved piezoelectric element which detects the acoustic signal. The signal is then amplified by an in-head preamplifier before being interfaced with the measuring system at the end of the umbilical. The head also contains a temperature sensor and an energy monitor system to check on the energy of the diode laser pulses. The entire head has been designed to an Ex-d specification in consultation with SIRA. This system is scheduled for offshore testing this year.

3 DISCUSSION

The photoacoustic technique although it has been in existence for one hundred years it has not previously been deployed in the manner described above. This is because the recent advances in technology have generated components which are very well suited to pulsed laser photoacoustic sensors. At this time, the sensor has been tested in the laboratory and at Orkney (ERT) and thus far the results are generally good. It is clear that the real test of the system will be from extended offshore testing to determine the true operational envelope and that is the next stage of development.

4 ACKNOWLEDGEMENTS

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5 PUBLICATIONS

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Hodgson, P.; Quan, K.M.; MacKenzie, H.A.; Freeborn S.S.;, Hannigan J., Johnston, E.M.; Greig, F.; Binnie, T.D.; "Application of Pulsed Laser Photoacoustic Sensors in Monitoring Oil Contamination in Water", Sensors and Actuators B , 29, 339 (1995)

A pulsed photoacoustic instrument for the detection of crude oil concentrations in produced water
S S Freeborn, J Hannigan, F Greig, R A Suttie and H A MacKenzie.
To be published in the November issue of *Review of Scientific Instruments.*