Development of the ANALOX Hyper-Gas™ Diving Bell Monitor

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Following an incident in the North Sea in which two divers showed signs of becoming anaesthetised following contamination of the diving bell internal environment, by volatile hyrdocarbons from condensate accidentally brought back to the bell, Unimed Scientific Limited was contracted to lead the development of a suitable monitoring device which would alert the divers to such a problem. The project was funded by a consortium of companies and organisations concerned with the offshore oil industry.

A Sponsor Group made up of representatives of the sponsors worked with USL and with the manufacturers, Analox, to produce suitable equipment using infra red technology. The device is in 2 parts, a bell unit and a topside repeater. The bell unit is located in the bell and is permanently switched on. In the event of volatile narcotic levels in the bell rising to a selected threshold level an alarm sounds in the bell warning bell occupants to stay on, or go on to, breathing apparatus. In a normal installation this is connected to the topside repeater to which it relays information at predetermined intervals of time. Data is stored and in the event of an incident information about signal levels, depth and tempaerature during the previous several hours can be downloaded to a computer. Following an alarm the previous 12 hours data can be downloaded to gain information about the development of the incident. The risk of false alarms is extremely low as there is a difference of several decades between the normal levels of narcotics in an uncontaminated diving bell and the level at which the divers would begin to suffer ill effects.

Prototype testing resulted in small changes to the design to ensure satisfactory function with minimum input from bell occupants. The equipment has now been approved for use in diving bells and is in commercial production.

CONTENTS

iv

1.0 INTRODUCTION

Early in 2000 Unimed Scientific Limited was tasked to provide financial and scientific management of a project for the development of equipment which would be capable of continuously monitoring the levels of volatile hydrocarbons in diving bells. This report deals with the scientific and technical details of the project.

1.1 BACKGROUND

In 1997 the whole North Sea diving industry became concerned about the danger of narcosis in divers in the event of contamination being carried into the diving bell during operations at dirty sites. The trigger for the concern was an incident in which 2 occupants of a diving bell showed all the signs of rapidly developing anaesthesia following the return of one diver from working on a condensate pipeline where there had already been evidence that the isolation procedure had not been successful. Luckily at the stage when they could still function they realised something was wrong and recovered the second diver who acted quickly, flushed the bell and put the two affected divers onto breathing apparatus. Their recovery was complete but the incident sounded a timely alarm.

That accident happened on a pipeline which was in use, but activities in the North Sea are entering a new phase in that many installations which are no longer required have to be cleared away or made safe. Many more operations will be undertaken at sites which can be considered as contaminated and where ensuring diver safety becomes more difficult. In addition the Erika incident off the coast of France, with the subsequent clean-up operation in 2000, highlighted the great risks of contamination to which divers might be exposed.

The presence of a detector in the bell, specifically set to monitor the level of volatile narcotics and to sound an alarm if levels are increased, would alert divers to remain on, or go onto, breathing apparatus.

2.0 SCIENTIFIC BACKGROUND

For obvious reasons little attention has been given to determining the anaesthetic potency of compounds arising from the contamination likely to be found in the oil industry. The major effort has been applied to compounds of use, or likely to be of use, in clinical anaesthesia. However a study of the anaesthetic properties of organic series, for example the alkanes, is a useful tool in the evaluation of the various theories of mechanisms of anaesthesia. It was the spin-off from this kind of work which provided enough information to make this project possible.

This research has shown that within a chemical series such as the alkanes (Lui et al 1993) or alkanols (Fang et al 1997) the anaesthetic potency increases with molecular weight, a lower partial pressure is required to give anaesthesia with the higher molecular weight compounds. Saturated vapour pressure decreases with increasing molecular weight and does so to a greater extent than the decrease in anaesthetic partial pressure. Thus the alkanes up to and including octane (molecular weight 114) have a sufficiently high vapour pressure to cause anaesthesia, from nonane and higher (molecular weight 128) saturated vapour pressure, at "normal" temperatures, is below anaesthetic partial pressure. Given the vast number of volatile organic compounds which could be present in crude oil, condensate and drilling muds this project becomes possible only because we can ignore all heavier compounds.

This still leaves a lot of compounds to consider, many of which have no recorded anaesthetic dose. In the end we have had to take a purely pragmatic approach but an approach which leaves it possible to take account of new knowledge should it ever be forthcoming.

2.1 ANAESTHETIC LEVELS OF VOLATILE HYDROCARBONS

2.1.1 Anaesthetic partial pressures

Table 1 lists minimum inhaled partial pressures (MIC) required for anaesthesia derived from the work of Fang et al (1996) and Liu et al (1993) together with the saturated vapour pressures. The latter values have been taken either from the experimental work of Liu et al or calculated from the equation:

$$\log_{10} P = -\frac{0.05223a}{T} + b$$

where a and b are constants published in the Handbook of Chemistry and Physics and T is the absolute temperature.

Also listed in Table 1 is the ratio of anaesthetic partial pressure to saturated vapour pressure. Once this ratio exceeds 1 the compound cannot exist at a sufficiently high vapour pressure to give anaesthesia. Saturated vapour pressure has been quoted for $30^{o}C$ that being approximately the temperature at which the diving bell is kept in heliox diving.

Anaesthetics are additive so that any given level of anaesthesia could result from either a single compound reaching the partial pressures quoted in Table 1 or from a mixture of compounds each at a fraction of the pressures quoted. This means that for the diving industry, where the contamination is likely to be by a complex mixture of compounds, anaesthesia is more likely to result from several compounds each at a relatively low level.

Such evidence as exists from experimental work on animals and humans suggests that higher doses of anaesthetic are required to reach a given end-point of anaesthesia at higher pressures. This reduction in anaesthetic potency appears to be due to the pressure reversal of anaesthesia. Anaesthetics are believed to have their affects by changing the structure and function of membranes within the body, pressure appears to reverse these changes and/or reverse the effect of the changes. (Simon and Bennett 1980, Wardley-Smith and Halsey 1980). Whatever the mechanism, the pressure reversal of anaesthesia means that any device set to respond to a particular level of contamination will be safer at higher pressures.

Table 1

Partial pressure required for anaesthesia

and saturated vapour pressure at 30°C (bar)

Compound	Vapour Pressure (bar)	Anaesthetic Pressure (bar)	Ratio
methane	Gas	9.9	
ethane	38.2	1.59	**0.042**
propane	8.5	0.940	**0.111**
isobutane	2.12		
n-butane	2.12	0.345	**0.163**
isopentane	0.618		
n-pentane	0.618	0.127	**0.206**
methylpentanes	0.325		
n-hexane	0.161	0.047	**0.292**
methylhexanes	0.103		
n-heptane	0.042	0.020	**0.476**
n-octane	0.019	0.017	**0.895**
n-nonane	0.0054	0.011	**2.04**
n-decane	0.0028	0.014	**5.00**
cyclohexane	0.136	0.045	**0.329**
methylcyclohexane	0.073		
benzene	0.120	0.017	**0.142**
toluene	0.045	0.009	**0.200**
o-xylene	0.011	0.0064	**0.582**
m-xylene	0.014	0.0071	**0.507**
p-xylene	0.015	0.0078	**0.520**
ethylbenzene		0.007	
cyclopentane		0.059	

From the point of view of diver safety anaesthesia is not the only end point to be considered. It is a general rule that prior to anaesthesia there is a stage of hyper-excitation. The pattern of behaviour due to alcohol consumption is a reasonable model. The victim losses the ability to take rational decisions and to make co-ordinated movements thereby losing the ability to look after himself. This can happen at levels considerably below anaesthetic level. There are some published numbers; from Fang et al (1996) 3 mbars of toluene, 33% of anaesthetic level, leads to hyperactivity, 0.9 mbars xylene, around 13% of anaesthetic level, causes tremors which can seriously impair purposeful actions. For benzene 7.4 mbars, 44% of anaesthesia, cause uncontrolled jerking of limbs, 22 mbars of cyclohexane, 52% of anaesthetic level, causes convulsions.

The wide range of anaesthetic levels and the sub-anaesthetic effects together with the large number of potential narcotics are all factors which contribute to the complexity of the project.

2.1.2 Volume of contamination which would give dangerous levels

The saturated vapour pressure (SVP) is the maximum partial pressure of a compound which can exist at a given temperature and that pressure is only reached if there is sufficient liquid to vaporise. Saturated vapour pressure is usually only achieved when the vapour coexists with the compound in the liquid phase. This raises the question as to what volume of the liquid compound is required to achieve SVP in a diving bell, how much contamination would have to be brought back to the bell.

The molecular weight of a liquid vaporises to 22.4 litres of vapour when measured at standard temperature and pressure (STP) which is 0°C and 1 standard atmosphere, 760 mmHg or 1013 mbar. At 30°C 22.4 litres becomes 24.86 litres and this is distributed into the volume of the diving bell. Most diving bells have a volume somewhere between 4.5 and 6 cubic metres. Thus the molecular weight of a compound will vaporise to become between 0.41 and 0.55% of an atmosphere in a bell at 1 atmosphere. This gives a partial pressure of between 4.14 and 5.52 mbar.

In a diving bell at any higher pressure the partial volume due to the vapour will be reduced in proportion to the increase in pressure but the partial pressure of the vapour will be as at 1 atmosphere. Table 2 lists the weight of each compound which would be required to raise the vapour partial pressure in the diving bell to anaesthetic level.

Table 2
Mass of compound required to produce anaesthetic partial pressure
within diving bell (g)

	Bell volume 4.5m^3	Bell volume 6m^3
methane	gas	gas
ethane	8,641	11,522
propane	7,493	9,990
n-butane	3,625	4,833
n-pentane	1,653	2,209
n-hexane	732	976
n-heptane	362	483
n-octane	351	468
cyclohexane	682	909
benzene	240	320
toluene	150	200
o-xylene	123	164
m-xylene	136	182
p-xylene	150	200
ethylbenzene	135	179
cyclopentane	748	998

These figures are a little misleading because it is unlikely that contamination would ever be a single compound but would in fact be the complex mixture of compounds which the industry is dealing with.

2.2 POTENTIAL CONTAMINATION LEVELS

One of the main problems encountered in this project was that of getting reliable information about the composition of the vapour phase above likely contaminants. This requires an analysis of the headspace above the liquid or seabed sediment. Samples of seabed mud from the site of dirty operations are usually brought to the surface in containers which are not gas tight. USL has been asked to carry out analysis on samples in everything from an ice-cream carton to a urine sample bottle. By the time these samples reach the deck most of the volatile components have vaporised leaving apparently clean samples. The problem of bringing samples from the seabed site to the surface without loss of volatiles is one which has not yet been solved and which should be addressed in preparation for the clean up operations in the North Sea.

As a compromise for this project, we carried out headspace analysis on samples of crude oil and condensate which are routinely taken for analysis of composition. The laboratory which does that work made 2 samples available to USL. These had been transferred from the pressure vessel to a gas tight container at 1 atmosphere following analysis by the laboratory. Thus some of the lighter volatiles would have been reduced in concentration in the liquid but there was the possibility that enough remained to give a realistic assessment of the composition of the vapour phase which could exist in the contaminated diving bell. Table 3 gives the results for the whole range of compounds detected. Those marked * are compounds listed in Table 1, compounds for which we have information about anaesthetic partial pressures.

We were able to make a check on the loss of the lighter volatiles because the laboratory which handled the original samples analysed the vapour phase for the light-end compounds. Table 4 compares the results from the original laboratory with those obtained by USL on the decanted samples. For volatiles from i-butane and heavier the agreement is good except apparently for hexane. In fact the laboratory gave a value only for all C_6 compound lumped together whereas the USL result was only for n-hexane.

8

Table 3

Headspace analysis, partial pressure, mbar

	CRUDE	CONDENSATE
*Propane	203	149
Iso-butane	45	47
*Butanes	130	116
Iso-pentane	22	26
*n-pentane	23	29
*Cyclopentane	6.3	7
3-Methylpentane	1.7	2
*n-hexane	4.9	5
Methylcyclopentane	2	2
*Benzene	3	4
*Cyclohexane	0.8	0.5
Methylhexanes	0.4	0.3
*n-heptane	0.7	0.76
Methylcyclohexane	0.9	0.97
*Toluene	0.8	0.63
Methylheptanes		0.06
*n-octane	0.2	0.11
Ethylcyclohexane	0.06	0.02
*Ethylbenzene	0.1	0.04
*m,p-xylenes	0.16	0.12
*o-xylene	0.35	0.32
*n-nonane	0.06	0.04
Isopropylbenzene	0.06	0.04
Propylbenzene	0.06	0.05
1,3,5-trimethylbenzene	0.06	0.06
1,2,4-trimethylbenzene	0.06	0.03
1,2,3-trimethylbenzene	0.04	0.03

Table 4

Comparison two analyses, vapour pressures in mbar

	Condensate		Crude	
	Laboratory 1	**Laboratory 2**	**Laboratory 1**	**Laboratory 2**
Propane	288	149	441	203.2
i-butane	49.4	47.4	44.7	44.6
n-butane	114	115.6	129	130
i-pentane	26	26.5	20.6	21.8
n-pentane	28.3	29.2	23	22.9
C_6 or hexane	38.3	5.24[*]	23.7	4.9[*]

* this result is for n-hexane alone , see text.

Table 4 indicates that we can have confidence in the results from the headspace analysis given in Table 3 except for propane where there had obviously been some loss during the handling of the samples for the original analysis.

Table 5 lists the results of the headspace analysis for the compounds for which we have anaesthetic partial pressures but this time given as a proportion of the anaesthetic dose. The values for propane were taken from Laboratory 1 (Table 4). The values for iso- and n- butane, and for iso- and n- pentane were summed. The anaesthetic level for m,p xylene was taken as the average of the two values listed in Table 1. These few compounds, for which we know the anaesthetic dose, total in the vapour phase of the condensate and crude samples at almost twice what is required to give anaesthesia.

These results demonstrate the need for a system of continuously monitoring bell hydrocarbons; confirm that the conclusions drawn from the incident which caused this project to be initiated were probably correct and give some guidance about setting the levels at which an alarm should be sounded.

Table 5
Proportion of anaesthetic dose present
in vapour phase above samples

Compound	Condensate	Crude
propane	0.306	0.469
butane	0.472	0.507
pentane	0.433	0.354
hexane	0.106	0.104
heptane	0.038	0.035
octane	0.006	0.012
cyclohexane	0.011	0.018
benzene	0.235	0.176
toluene	0.070	0.089
o-xylene	0.050	0.055
m,p-xylene	0.016	0.021
ethylbenzene	0.006	0.014
cyclopentane	0.119	0.107
TOTAL	**1.87**	**1.96**

2.3 THE ALARM LEVELS

The final details about where to set the level which causes the alarm to sound could only be taken once more was known about the response of the equipment to the different compounds and will be dealt with in a later section of this report. There are several general conclusions which can be drawn at this stage.

In an ideal world it would be possible to take samples under pressure from the work site in advance of beginning the job, get a headspace analysis carried out and therefore know the spectrum of compounds which form the potential source of danger. In the present situation, when there is no satisfactory sampling technique available, the ideal cannot be achieved. The alarm level has to be determined with reference to the values given in Table 5.

It was originally thought that it would be appropriate to set the alarm to sound when one particular compound reached a fixed proportion of anaesthetic level for that compound. Initially something like 10% was considered appropriate. This would allow for the fact that several compounds might be contributing, each at a level considerably below anaesthetic level. Obviously for any job where it was known that possible contamination would be by only one or two identified compounds this approach would be suitable. Once the relative sensitivity of the device was known it became apparent that taking this approach, setting the alarm at a percentage of anaesthetic concentration for one compound, would make it possible for some compounds to exceed danger levels before the alarm sounded.

For the present situation, in the present state of knowledge, a better approach is to set the alarm to sound when the total response to a spectrum of compounds exceeds a chosen level. As an example, Table 6 lists the percentage of anaesthetic level reached for each compound in the proportions found in the analysis of crude, as given in Table 3, when the total of these compounds equals 10% of anaesthetic level.

Using the anaesthetic levels given in Table 6 and the mass which would be required to cause anaesthetic levels to be reached in a diving bell, Table 2, it is possible to calculate the volume of crude which could cause the alarm to fire if the alarm level were set in this way. The density of the crude sample was 814.7 Kg/m^3. In a 4.5 m^3 bell 317 ml would vaporise to alarm levels, in a 6 m^3 bell 423 ml would be required. From the information given in section 2.1 about the effects of sub-anaesthetic levels, it is apparent that divers could suffer reduced ability to look after themselves with contamination by as little as 100 to 150 ml of liquid.

Table 6

Levels of each compound so that total is 10% anaesthesia,

proportions as in headspace analysis of crude.

	% Anaesthetic level	**Concentration (ppm)**
propane	2.4	22477
butane	2.6	8920
pentane	1.8	2293
hexane	0.5	250
heptane	0.2	35.7
octane	0.1	10.2
cyclohexane	0.1	40.7
benzene	0.9	152.9
toluene	0.5	40.8
o-xylene	0.3	17.8
m,p-xylene	0.1	8.2
ethylbenzene	0.1	5.1
cyclopentane	0.8	457
TOTAL	10.0	

2.4 NORMAL HYDROCARBON LEVELS IN DIVING BELLS

USL has several years experience of gas analysis on samples drawn from diving systems. Table 7 is taken from the database containing all the results for diving bells. It shows the average concentration of compounds during 2001 and 2002 for diving bells working in the North Sea. The xylene levels are a little higher than usual as the average included samples from 2 bells taken immediately after repainting. Comparison of the values in Table 7 with those in the last column of Table 6 show that the potential for false alarms is low.

Table 7
Concentrations normally found in diving bells (ppm)

	Concentration
propane	0.017
butane	0.004
pentane	0.098
hexane	0.028
heptane	0.005
octane	0.004
cyclohexane	0.014
benzene	0.022
toluene	0.088
o-xylene	0.734
m,p-xylene	2.4
ethylbenzene	0.050

3.0 DEVELOPMENT OF THE DEVICE

All of the compounds of interest in this project absorb infra red radiation and Unimed Scientific Limited commissioned Analox, a company with considerable experience in building infra red equipment, to develop the device. Analox's task was to design and develop an infra red hyperbaric sensor to be built into equipment suitable for installation into a diving bell. The instrument is required to detect hydrocarbons and alarm before the concentration (total partial pressure) of hydrocarbons reaches a dangerous level.

Key development tasks included :

1   development of an infra red sensor able to;

          operate in pressures up to 60 bar

          operate in high humidity and a range of temperature conditions

          provide a fast response to the presence of hydrocarbons

2   produce equipment suitable for use in the diving bell taking the following into account;

          the hazardous nature of the gases involved (for many of the gases the anaesthetic level exceeds the Lower Explosive Limit (LEL) concentration at lower pressures)

          the limited space in the bell

The functional requirements of the instrument was determined by a Sponsor Group drawn from all sectors of the industry. This ensured that the equipment designed meets the user's needs.

3.1 INFRA RED TECHNOLOGY

The basic principles behind infra red technology are as follows. Many gases absorb infra red energy to different degrees and in different areas of the infra red spectrum. A sensor can be developed to detect this energy by using a gas sample chamber, with an infra red source at one end and an infra red receiver (or detector) at the other. By fitting an interference filter in front of the infra red receiver the sensor can be tuned to detect specific gases. The gas concentration can be determined by measuring the amount of infra red light reaching the IR receiver. A decrease in signal produced by the detector indicates the presence of the target gas.

The design of infra red sensors can vary greatly. Variables include single beam, dual wavelength, dual beam, folded pathlengths, gold plated benches and/or heated sensors. Each of these designs has advantages and disadvantages and normally the selection is made to suit the particular application.

The main problem areas associated with developing infra red sensors are as follow :

signal to noise ratio

temperature changes causing drift in the sensor and electronics

cross sensitivity to gases other than those of interest

In addition, for this particular application, the effects of changing pressure must be taken into account.

3.2 ABSORPTION SPECTRA

3.2.1 Alkanes

Figure 1 shows the absorption spectra for alkanes. All show a bimodal pattern of absorption within the range 3.2 to 3.6 μm. Filter selection to this range of wavelengths should therefore enable detection of the alkanes. Figure 2 shows the response to different concentrations of five compounds. The concentration corresponding to 10% of the anaesthetic level of each gas is marked as a vertical line on each data line.
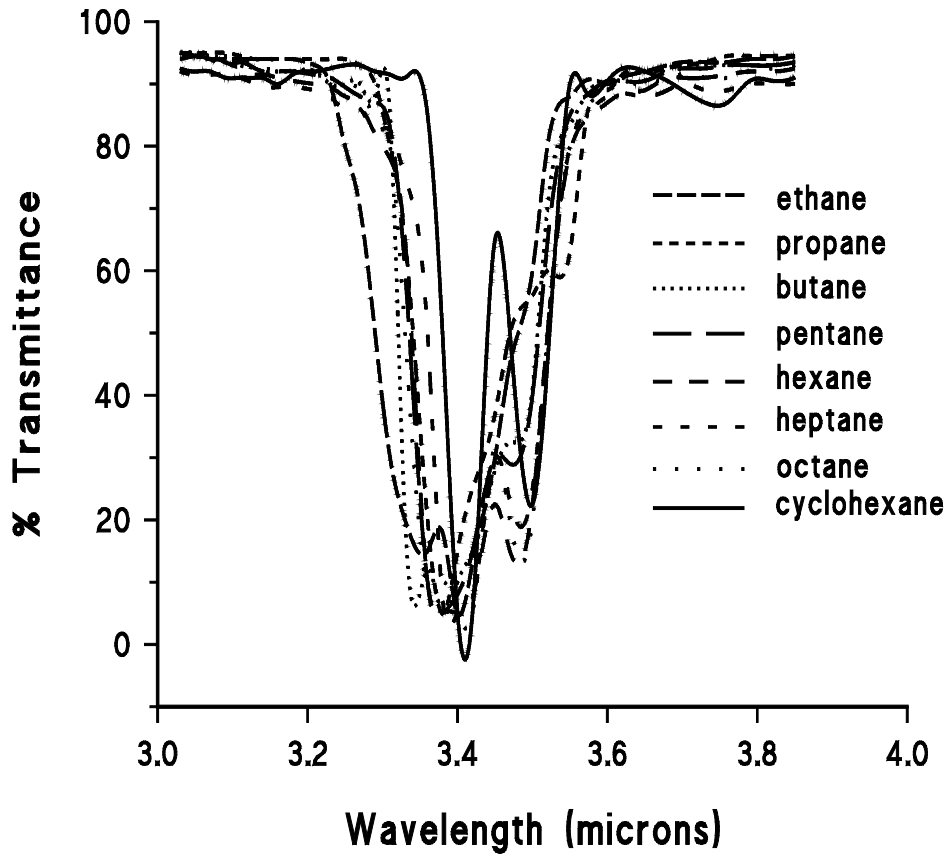
Figure 1
Infra red spectra

Ten percent of anaesthetic level was the level which was initially considered appropriate for the alarm setting. The response is reasonably linear over the range of concentrations and in fact is very similar for identical concentrations of all five. For example 2000 ppm of any of the compounds gives a reading of around 2200 ADC bits for each compound.
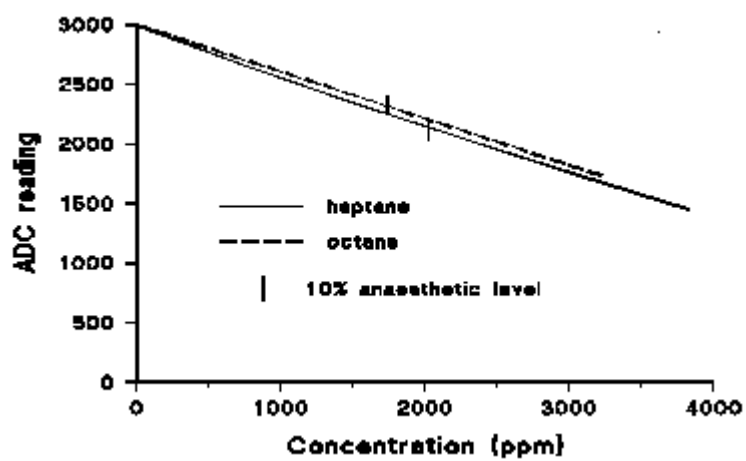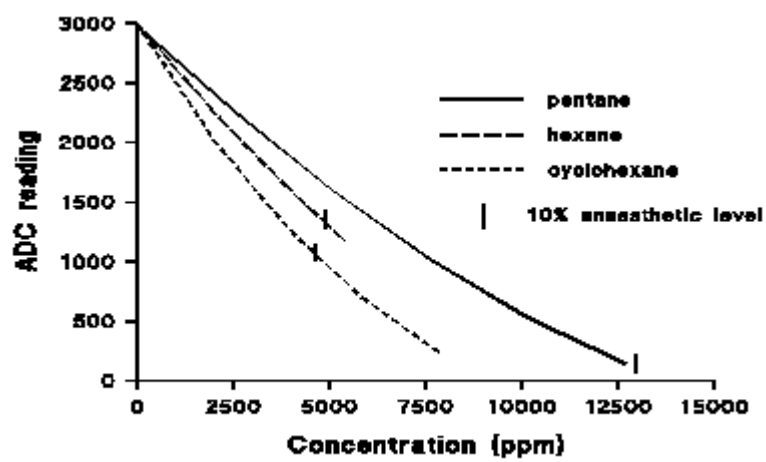
Figure 2
Infra red response

When redrawn with the concentration expressed as a percentage of the proposed alarm level, figure 3, the wide range of relative response becomes apparent. If the alarm is set to sound when the output reaches 10% of anaesthetic level for octane it will also sound when pentane is at less than 20% of that, i.e. less than 2% of anaesthetic level.
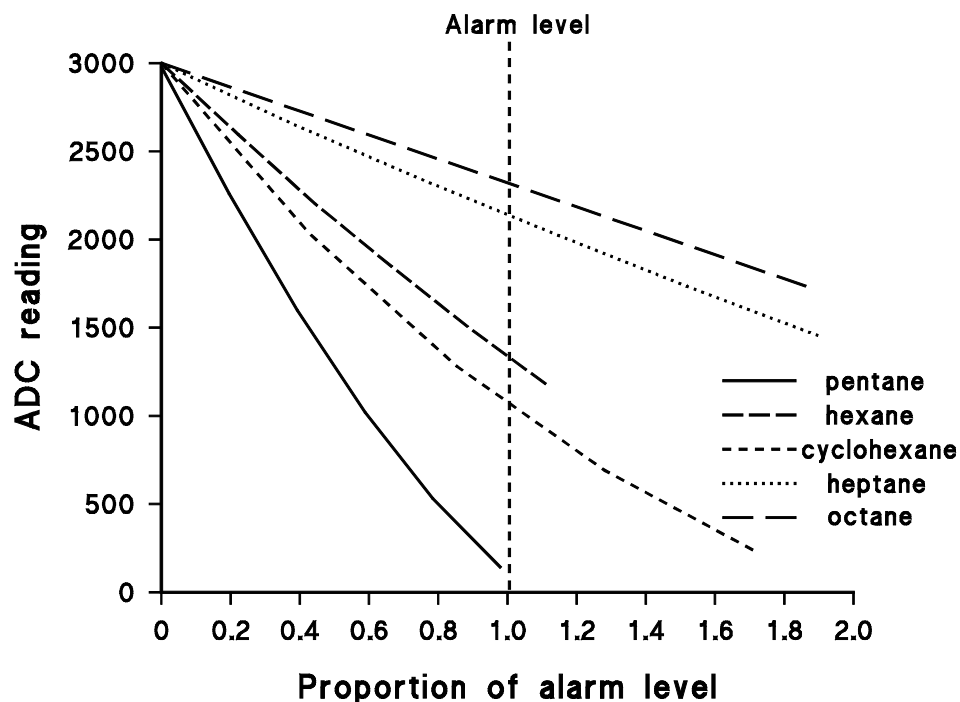

Figure 3
Data from figure 2 replotted as proportion of 10% anaesthetic level

To overcome this problem the Sponsor Group decided the alarm level should be set to reflect the additive effect of the common hydrocarbons present rather than the individual gases. This introduced the need to have information about the relative partial pressures of the different compounds likely to be in the vapour phase of contamination which has been described in Section 2.2.

3.2.2 Aromatics

The aromatic hydrocarbons absorb infra red energy in different areas of the infra red spectrum from alkanes. This introduces the possible need to have 2 different sensors, one for alkanes and one for aromatics. The degree of absorption of infra red by the aromatic hydrocarbons is

19

also very low compared to the alkanes. Poor infra red absorption makes it necessary to use a high level of amplification for the aromatic bench which will compound the problems of signal to noise ratio and temperature drift. The sensor developed to give the maximum detection of alkanes showed poor response to aromatics. Increasing the infra red path length to allow a greater volume of gas within the sample chamber did not lead to a sufficient improvement to make the signal size comparable to that for the alkanes; the disparity in sensitivity remained too great.

Aromatic hydrocarbons show their greatest infra red absorption above 11 microns and the possibility of using a second bench operating at this wavelength was explored. The appropriate filters were sourced and a long path length sensor developed. However, at the concentrations required, the level of infra red absorption was still too low to produce a stable signal. Again the high level of amplification required meant that temperature drifts in the electronics would be amplified possibly to levels which would cause the alarm to sound. Another strong argument against using 2 benches was the problem of determining the relative importance of the signal from each sensor. This was particularly difficult given that a straight summation of the total gases was what was required for this particular purpose. (See Section 2.1).

The solution finally came with the use of a special filter which effectively reduced the disparity between sensitivity to alkanes and to aromatics in the 3 - 3.5 μm range. There is still a range of sensitivity, Table 8 shows the relative sensitivities for the compounds tested. However for use in diving, where the contamination will contain a range of compounds from both groups and where the alarm level is to be determined by the summation from all compounds, this could be made to work. For an application where, for example, contamination would be entirely by aromatics, the alarm level setting would have to be quite different from that for the diving industry.

3.3 RESPONSE TIMES

As vaporisation of hydrocarbons is rapid and the onset of anaesthesia evident within one or two breaths the response time of the device must be very short. Many infra red detectors are fitted with a membrane to protect the sensor optics from contamination by dirt/dust and water vapour. Tests using several different membranes showed that they slowed the diffusion of gas into the cell and resulted in 90% response times of the order of minutes.

The sensor was reconstructed to remove the need for a membrane but the response time remained high when the bell gas was left to enter the sensor by diffusion. It was apparent that it would be necessary to generate a flow through the equipment. This was tried first with a

pump which brought the response time down to less than 10 seconds. However the possibility of pump failure led the Sponsor Group to rethink as the intention was that the device must require minimal attention once installed. It was decided that the device could sit in the bell gas sample line which has a continuous flow drawn through it due to the pressure differential between the bell and the gas analyzers on the surface. It has proved possible to split the total flow through the line to give a flow to the hydrocarbon monitor which matches that which was obtained from the pump. A flow alarm alerts to an inadequate flow.

3.4 SELECTION OF ALARM LEVELS

Considerable thought was given to the determination of a suitable level which would cause the alarm to sound. Because of the effects of sub-anaesthetic levels and because there may be more compounds which can contribute to narcosis but for which we do not have anaesthetic levels it would be wise to err on the side of caution and set the alarm at a low level. The argument against this is the risk of false alarms which would be costly for the industry and probably result in the equipment being switched off or alarms ignored. The values in Table 7 suggest that the risk of false alarms will be low. The prototypes were prepared so that the alarm would sound when the signal reached a size equivalent to a 10% anaesthetic level for the compounds available for testing. This can be adjusted by the manufacturer and should be adjusted for any application where there are only one or two compounds as possible contaminants.

Equally the alarm level can be easily adjusted if, the in the light of operational experience, it is set too high. It is planned that, in operational use, should the alarm sound gas samples will be drawn into cylinders and sent for a full hydrocarbon analysis. This will allow the build up of information about the levels and the relative concentrations of compounds to which the device has to respond. The routine monitoring of bell environment, required during diving operations in the Norwegian sector of the North Sea, continues to give information about the normal levels of hydrocarbons.

The compounds for which the relative sensitivity of the detector has been measured are propane, butane, pentane, hexane, cyclohexane, benzene and xylene. As discussed in section 2.3, rather than setting the alarm to a particular level of a single compound, a safer approach is to set to a number of compounds reaching a particular level. An appropriate level has been taken as 10% of anaesthetic level which means that the alarm will sound before levels which might reduce the ability of the divers to take sensible actions.

Table 8 lists the sensitivity, given as the reading for 10,000 ppm, for the seven compounds expressed relative to the sensitivity for propane. Also listed is the proportion of anaesthesia for each compound when the total adds up to 10% of an anaesthetic dose, both for crude and condensate as given in Table 3 but with the value for propane taken from Table 4 Laboratory 1. Iso- and n-butane, iso and n- propane and all xylenes have been taken together for butane, propane and xylene. The final 2 columns give the contribution to the total reading expected from each compound, together with the total reading.

Table 8
See text for details

	Sensitivity	Anaesthesia		Reading	
		Crude	**Condensate**	**Crude**	**Condensate**
propane	1.01	0.0275	0.0188	2.612	1.784
butane	1.26	0.0298	0.0290	1.293	1.259
pentane	1.44	0.0208	0.0266	0.380	0.486
hexane	1.61	0.0061	0.0652	0.046	0.049
cyclohexane	1.3	0.0010	0.0007	0.003	0.002
benzene	0.30	0.0104	0.0144	0.005	0.007
xylene	0.33	0.0045	0.0041	0.007	0.006
TOTAL		**0.100**	**0.100**	**4.346**	**3.593**

It is possible, if only one volatile is present, to reach anaesthetic levels before the alarm sounds. For example, if for general North Sea diving purposes, the alarm were set at the average of 4.35 and 3.6, i.e. accepting that both crude and condensate will contribute to contamination, then in an environment where only benzene vapour is present it can reach almost 8 times anaesthetic level before the alarm sounds. For an environment where only one or two compounds can contribute to the contamination an appropriate alarm level must be set.

4.0 PROTOTYPE TRIALS

The prototype equipment was installed in diving bells on four diving support vessels over the course of six months. With the exception of the first prototype test the units were left to run for a period of several weeks. The feedback from each installation allowed the equipment to be refined and modified in a way which ensured that it was acceptable to the users and would remain trouble-free during use.

The intention was that the equipment would be installed in the bell and left to run. In the event of an alarm sounding samples of the bell atmosphere would be drawn into previously evacuated gas cylinders and sent for full analysis for volatile hydrocarbons. One of the prototype tests was carried out at a location where the problems of contamination could be higher than normal. For this test, in the event that there was no alarm the cylinders were to be filled towards the end of the period of the test and returned for analysis.

Communication between the bell unit and the topside repeater is digital and should be by completely screened hard wire links in the bell umbilical. However the first prototype test drew attention to the fact that often wiring within the umbilicals has been modified so that screening is less than perfect. In the case of the first prototype the transfer of information from the bell unit caused interference on audio and video communication systems. This problem was dealt with in two ways, the prototypes were modified to reduce the possibility of interference and, because the time required to actually send the information is of the order of milliseconds, intermittent transmission is used. In the final version information is transmitted only once every 30 minutes when there is no alarm. When the alarm sounds the information will be transmitted once every 30 seconds. These short bursts should not cause detectable interference problems even in a bell which has inadequate screening.

On the second vessel the bell unit became waterlogged as water ran back down the gas line. This led to the inclusion of a water trap in the flow exit line of the bell unit. At the same time waterproof membranes were fitted on both the inlet and outlet lines to prevent condensate running back to the detector. The heat generated by the infrared source prevents condensation between these membranes.

During the course of the second, third and fourth prototype tests sample cylinders were filled. The results of analysis for all 5 cylinders given in Table 9 for the compound which were detected. The full range of compounds covered by the analysis is not listed.

Table 9

Compounds detected in samples taken during prototype testing

Component	CAS	ppm	ppm	ppm	ppm	ppm
Methane	74-82-8	11.6	55.1	128.7	0.000	0.000
Ethane	74-84-0	0.030	0.140	0.045	0.000	0.022
Ethene	74-85-1	0.020	0.040	0.069	0.002	0.000
Propane	74-98-6	0.010	0.110	0.023	0.000	0.023
i-Butane	106-97-8	0.000	0.040	0.015	0.000	0.003
n-Butane		0.000	0.090	0.008	0.000	0.011
Trans-2-butene		0.010	0.000	0.000	0.000	0.005
1-Butene	25167-67-3	0.010	0.020	0.004	0.000	0.006
i-Butylene		0.030	0.050	0.024	0.000	0.000
2, Methyl-butane	78-78-4	0.000	0.060	0.000	0.000	0.000
n-pentane	109-66-0	0.020	0.080	0.047	0.000	0.011
Cyclohexane	110-82-7	0.010	0.040	0.033	0.003	0.183
2-Methyl-Pentane	96-14-0	0.010	0.040	0.000	0.000	0.000
3-Methyl-Pentane	96-14-0	0.010	0.030	0.000	0.000	0.000
n-Hexane	110-54-3	0.000	0.060	0.000	0.000	0.000
Isoprene	78-79-5	0.060	0.150	0.185	0.000	0.000
n-Heptane	142-82-5	0.010	0.030	0.005	0.000	0.000
Benzene	71-43-2	0.020	0.020	0.011	0.008	0.034
Toluene	108-88-3	0.020	0.050	0.024	0.004	0.124
Ethyl-Benzene	100-41-4	0.010	0.030	0.013	0.000	0.000
m+p Xylene	108-38-3/106-42-3	0.020	0.080	0.030	0.000	0.000
o-Xylene	95-47-6	0.010	0.040	0.018	0.000	0.000
n-Octane	111-65-9	0.000	0.010	0.001	0.000	0.000
n-Nonane	111-84-2	0.000	0.020	0.004	0.000	0.000
1,3,5 Trimethyl-Benzene	108-67-8	0.020	0.040	0.019	0.000	0.000
1,2,4 Trimethyl-Benzene	95-63-6	0.040	0.060	0.017	0.000	0.000
C9 Aromatics		0.320	0.350	0.148	0.000	0.000
Limonene	5989-27-5	0.460	0.880	0.152	0.125	0.000
Dichloromethane	75-09-02	0.000	0.000	0.010	0.000	0.000
Chloroform	67-66-3	0.050	0.440	0.036	0.000	0.000
Tetrachloroethylene	127-18-4	0.000	0.060	0.003	0.000	0.000

Three of these samples include a compound which has been used as a clinical anaesthetic, chloroform. The minimum anaesthetic level for this is about 5mbar. Taking all the compounds for which we have values for anaesthetic levels the total contamination for the 5 samples in Table 9, expressed as a percentage of anaesthetic level, are 0.0002, 0.0015, 0.0007, 0.00001 and 0.0002%. These values are in agreement with the fact that the digital read-out from the monitor for these trials was indistinguishable from zero.

Figure 4 shows the data recovered at the end of two of the prototype trials showing that the total hydrocarbon readings were well below alarm level. The dotted lines record the pressure in the diving bell in bar.
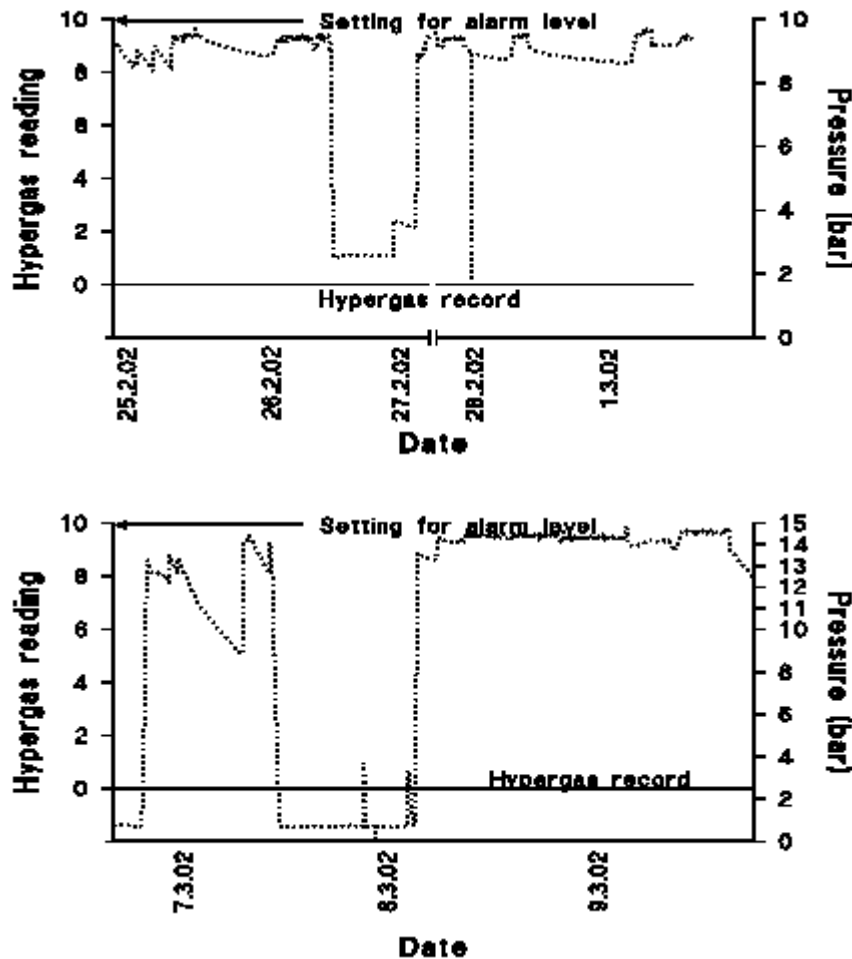

Figure 4

5.0 THE FINAL DESIGN

The Analox Hyper-Gas system is designed to monitor hydrocarbon gases in diving bells to alert divers to contamination of bell atmosphere at depths down to 600 metres.

The system consists of two units:

1   a Hyper-Gas Bell Monitor containing the infra red hydrocarbon sensor and a depth sensor

2   a Hyper-Gas Topside Repeater

Both units are powered by a 24V DC supply and they are connected together via the dive bell umbilical for communications. The Bell unit monitors and measures the total hydrocarbon content in the diving bell, updates its alarm indicators and transfers the information to the Topside Repeater which shows the same information at the surface.

It is assumed that the diving bell already has a gas sample line feeding bell atmosphere gas to the surface for analysis of permanent gases. This gas sample line is to be re-routed through the Bell Monitor. There is no gas connection to the Topside Repeater.

The Bell Monitor "sees" the total hydrocarbon content in the sample line. It is calibrated using a propane gas mix and sensitivity to other gases is determined relative to the sensitivity to propane. The range of the instrument has been designed to make it responsive to a typical mixture of gases which could be found in a contaminated diving bell as discussed in section 3.0

The Bell Monitor provides four indicator lights as follows:

OK   Flashes at regular intervals to show that the instrument is working and that the gas levels are below the pre-set alarm level.

Danger   Will flash if the hydrocarbon content in the sample gas exceeds the pre-set limit.

Sensor Fault Flashes in the event of an internal fault being detected.

Flow Alarm   Illuminates in the absence of a sample flow. This indicator must be OFF for the unit to be operating correctly.

An audible alarm will sound in the event of the hydrocarbon level exceeding the pre-set level. This can be muted but will sound again after 5 minutes if gas levels have not dropped to below the alarm level. Bell occupants must stay on breathing apparatus until the audible alarm has been silent for longer than the minimum time of 5 minutes.

The Hyper-Gas is fitted with a data logging facility. This logs the measured levels of hydrocarbons, the depth and the corresponding date and time. Once the logging capacity is exceeded the Hyper-Gas will automatically overwrite the oldest data. Data can be downloaded via the Topside Repeater onto a PC using the RS232 lead and the datalog retrieval programme.

5.1 BELL MONITOR

Figure 5 shows the Bell Monitor together with the water trap and pressure relief valve which are fitted between the outlet from the unit and the connection to the bell gas analysis line.
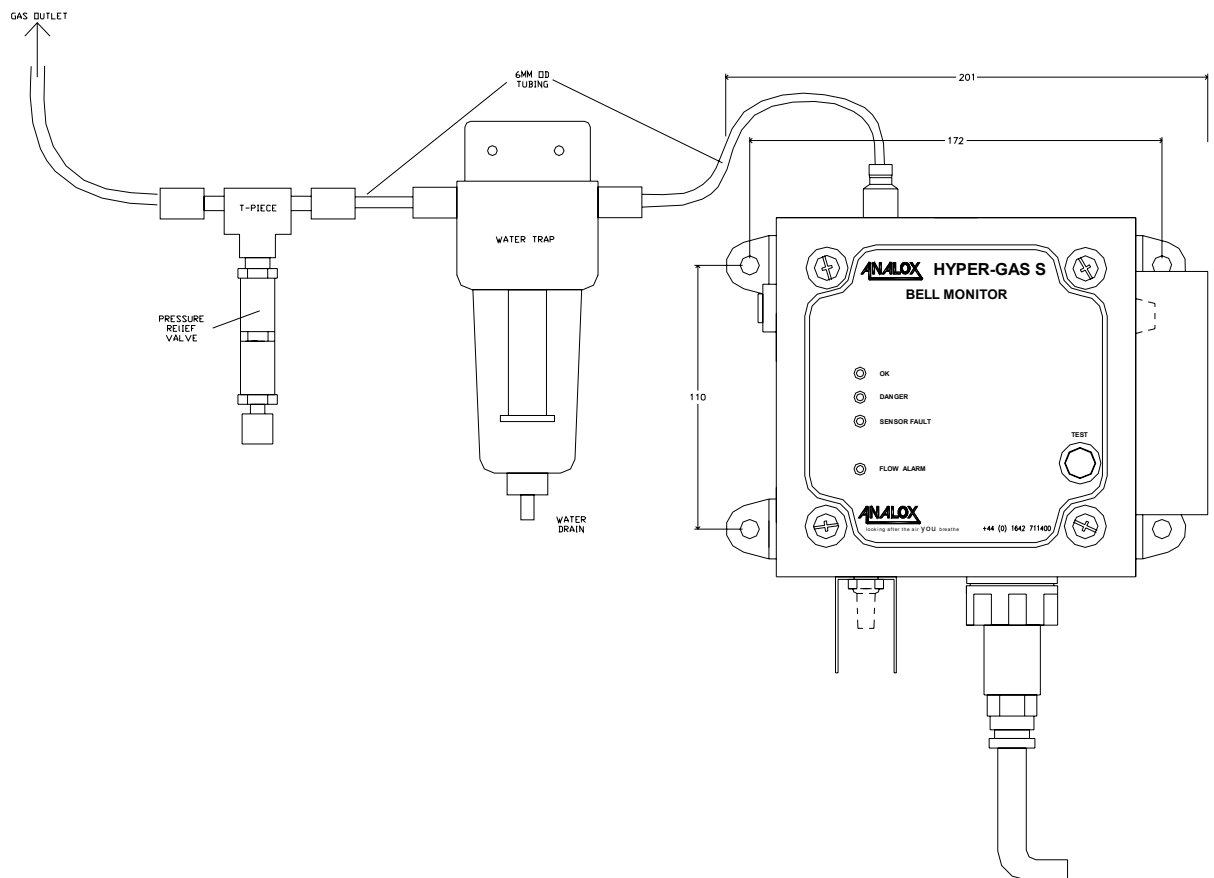

Figure 5

5.2 TOPSIDE REPEATER

The Topside Repeater is updated by the Bell Monitor and it shows the same information. It is fitted with an additional indicator, a "Bell Comms Alarm" which will illuminate if the 2 units are not communicating. Figure 6 shows the repeater unit.
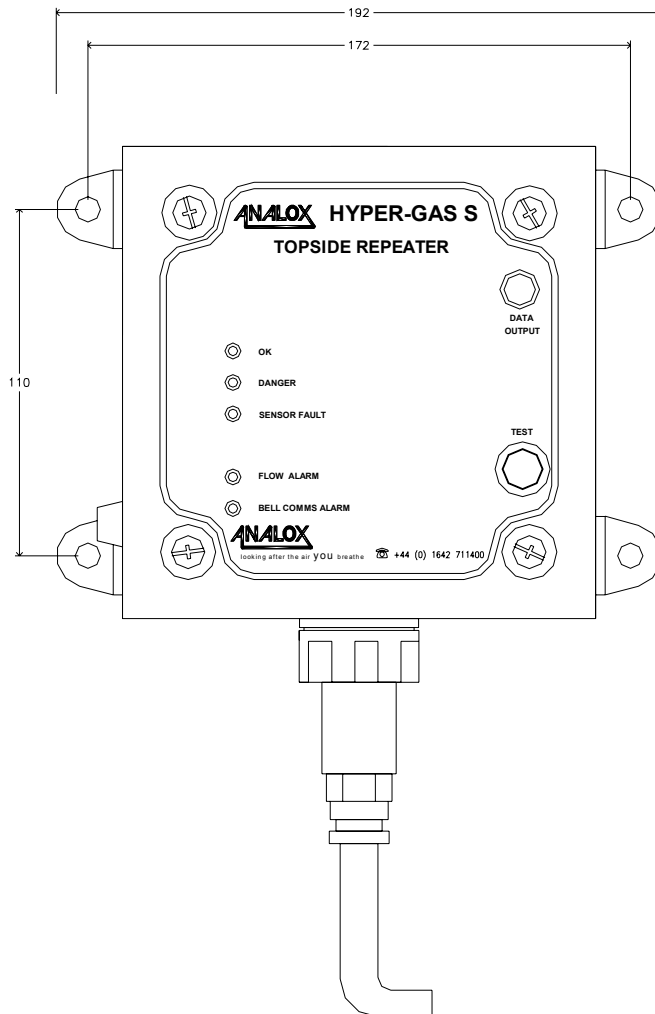

Figure 6

Tables 10 and 11 show the response of the Hyper-Gas as set for contamination by crude and by condensate.

Table 10

HYPERGAS ANALYSER RESPONSE TO CRUDE OIL

Based on the Headspace analysis of crude oil provided by USL

Gas	Head Space Actual %	100% Anaesthetic level of the gas	Anaesthetic Level % present in sample	How the analyser responds when calibrated to display in % A Head space gas
Cyclo-hexane	0.08	4.20	1.81	0.40
Hexane	1.09	4.70	23.23	7.25
Pentane	5.13	12.70	40.39	30.26
Butane	17.47	34.50	50.63	90.35
Propane	20.32	94.00	21.62	84.63
Xylene	0.05	0.15	34.00	0.07
Benzene	0.42	1.00	41.80	0.52
Total % A Present			**213.48**	**213.48**
Anaesthetic level of headspace gas			**10.00**	**10.00**

Responses to individual gas species at their 10% Anaesthetic levels when the Hyper-Gas is calibrated to read A values for crude head space analysis

Gas	Actual % Vol at 10% A level	Hyper-Gas reading
Cyclo-hexane	0.42	2.24
Hexane	0.47	3.12
Pentane	1.27	7.49
Butane	3.45	17.85
Propane	9.4	39.15
Xylene	0.02	0.02
Benzene	0.1	0.12

Note: Aliphatics above C6 were added to Hexane and Aromatics were added to Benzene

Table 11

HYPERGAS ANALYSER RESPONSE TO CONDENSATE

Based on the Headspace analysis of condensate provided by USL

Gas	Head Space Actual %	100% Anaesthetic level of the gas	Anaesthetic Level % present in sample	How the analyser responds when calibrated to display in % A Head space gas
Cyclo-hexane	0.05	4.20	1.14	0.29
Hexane	1.12	4.70	23.83	8.35
Pentane	6.20	12.70	48.82	41.08
Butane	16.29	34.50	47.22	94.67
Propane	14.94	94.00	15.89	69.9
Xylene	0.04	0.15	29.33	0.07
Benzene	0.49	1.00	48.80	0.68
Total % A Present			**215.04**	**215.04**
Anaesthetic level of headspace gas			**10.00**	**10.00**

Responses to individual gas species at their 10% Anaesthetic levels when the Hyper-Gas is calibrated to read A values for condensate headspace analysis

Gas	Actual % Vol at 10% A level	Hyper-Gas reading
Cyclo-hexane	0.42	2.51
Hexane	0.47	3.50
Pentane	1.27	8.41
Butane	3.45	20.05
Propane	9.4	43.98
Xylene	0.02	0.02
Benzene	0.1	0.14

Note: Aliphatics above C6 were added to Hexane and Aromatics were added to Benzene

Table 12

Power Source	External stabilised 18-30V DC supply with regulation better than ± 300 mV	
Operating Current	Topside Repeater	100 mA
	Bell Monitor	200 mA
Fuses	Topside Repeater	T250 mA
	Bell Monitor	T250 mA
Pressure Sensor	Analox pressure transducer with bridge output	
	Range	0 - 61 bar (600 msw)
	Accuracy	< 0.5% of range
Hydrocarbon Sensor	Analox infra red sensor	
	Range	0 - 30% Propane
	Accuracy (0 - midscale)	< 5% of range
	Accuracy (mid - fullscale)	< 10% of range
	Response time	Typically 10 - 15 seconds to alarm
Temperature	Operating	5°C to 35°C
	Storage	-20°C to 55°C
Dimensions	Bell Monitor	200mm(w)x215mm(h)x100mm(d)
	Topside Repeater	190mm(w)x160mm(h)x100mm(d)
Weight	Bell Monitor	< 2.5 kg
	Topside Repeater	< 2.0 kg

ACKNOWLEDGEMENTS

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