Oil-in-Water Monitoring – Where Are We Heading in the North Sea?

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1 INTRODUCTION

Oil-in-water has been traditionally measured by Freon extraction and then Infrared (IR) analysis. Due to the phase-out of Freon, the method and the whole monitoring regime has been under review for some time. Freon replacements and alternative monitoring methods have been the subject of much research and investigation. There have been a lot of activities from governmental bodies, industrial associations to individual operators in identifying a Freon replacement and / or an alternative analysis method.

Though the current official monitoring method is still the Infrared based method using Freon and/or Perklone, the establishment of the new ISO 9377-2 GC-FID method[1] has led Oslo-Paris Commission (OSPAR) seriously considering to recommend such a method as a reference method for the determination of oil content in produced water. A number of studies have already been carried out to see if such a method is suitable. A further study involving a considerable number of offshore installations has been taking place by the OSPAR to compare the old IR method and a modified version of the ISO 9377-2 GC-FID to finally confirm if such a method is suitable. However even such a method is recommended, for offshore routine monitoring alternative methods are still considered to be necessary.

Also OSPAR is currently preparing performance standards and reference methods for aromatics in produced water. To promote the process a workshop event was organised on 27-28 November 2002 on "setting performance standards for aromatic hydrocarbons in produced water" by the Danish Authority on behave of OSPAR. The Workshop was attended by all OSPAR countries. Both the need for performance standards and the feasibility of compliance to performance standards were extensively discussed.

This paper will provide an overview on how far we have come, what the current situation is and where we think things will be heading with regard to produced water oil content monitoring

2 CURRENT OIL-IN-WATER MONITORING AND MEASUREMENT

2.1 OSPAR Approved Oil-in-Water Analysis Reference Method

The current approved oil-in-water analysis reference method is based on an Infrared quantification detailed in the PARCOM Agreement 1997-16 [2]. It involves acidifying the samples (1 litre) to a low pH and then extracting the oil with two volumes of 1,2,2-trichloro - 1,1,2-trifluoroethane (also known as Freon 113) or tetrachloroethylene (also known as TTCE, perchloroethylene or Perklone). The extract is then treated with a Florisil to remove the polar components. The oil content is then determined by comparison of the infrared absorbance of the sample extract against that of the calibration standards prepared using specific crude oils.

The infrared quantification is made at wavelength of 2930 cm^{-1}, which corresponds to the CH_2 stretch vibration. Both single beam and non-scanning spectrophotometers and scanning spectrophotometers can be used. The oil content measured by this method is referred by OSPAR as the "dispersed oil".

Despite the PARCOM agreement on the analysis method, variations exist in the actual methods that have been used by the different nations in the North Sea region. The differences are mainly on how the standard solutions are prepared, whether to use two wavelengths or a single wavelength for quantifying the aliphatic part of oils, and also the different materials used to remove the polar components.

2.3 Discharge Limit in The North Sea and The Definition of Oil

In the OSPAR maritime area, no individual offshore oil and gas installations should exceed a performance standard for dispersed oil of 40 mg/l. This will be reduced to 30 mg/l by the end of year 2006[3].

Oil in the produced water discharge can be present in three forms

- **Dispersed**: in the form of small droplets (say in the range from 0.5 to 100 μm); both aliphatic and aromatic hydrocarbons can be contained in the dispersed oil
- **Dissolved**: such as BETX (benzene, ethyl-benzene, Toluene and xylene), and some of the PAHs (polycyclic aromatic hydrocarbons).
- **Free oil**: floating on the surface of water or in the form of large droplets that will settle out very quickly

When a produced water sample is analysed, all three forms of oils may be present and are extracted. But since the dissolved parts are predominately the aromatics, phenols and carboxylic acids, these are not included in the IR quantification of the OSPAR analysis method. The measured oil is therefore referred as the dispersed oil. In more accurate terms, the dispersed oil referred in the OSPAR Recommendation is actually the aliphatic part of the dispersed oil in the produced water. Dissolved aliphatic hydrocarbons in the OSPAR specified method are considered to be negligible.

When an IR quantification of oil is carried out using three wavelengths, the measured oil is referred to by OSPAR as the total oil. Here both aromatic and aliphatic hydrocarbons of both dissolved and dispersed that are extractable by the solvent (Froen or Perklone) are included.

2.4 The Role of Acidification and Florisil Treatment

In the OSPAR specified method it is stated that unless the sample is extracted on the day of collection, 5 ml of hydrochloric acid (1:1) is added to a one litre sample. The purpose of the addition of the acid is to preserve the sample against bacteria and also to dissolve any calcium carbonate, and iron oxide precipitate that the sample may have. Solid particles can cause troubles in the solvent extraction process in which it can help form and stablise emulsions and hinder the solvent / water separation.

However acidification of produced water sample can lead to the conversion of certain substances such as phenols and carboxylic acid from its dissolved, non-freon/Perklone extractable form to a dispersed and freon/Perklone extractable form. As a result, these substances may be included in the Infrared quantification. To make sure that these substances are not included in the analysis, the extract is then treated with a Florisil before Infrared analysis by passing the extract through the Florisil material. Florisil is a trade name for a prepared diatomaceous substance, mainly consisting of anhydrous magnesium silicate.

2.5 Current Oil-in-Water Monitoring Practices in the North Sea

Measurement of oil-in-water has two primary functions, firstly to ensure the performance of separation process and secondly for statutory reporting.

(a) Laboratory analysis

Up until recently, oil-in-water monitoring has been mainly carried out using Freon extraction and Infrared quantification. A number of portable instruments have been available [4]. The procedures are simple and instruments are relatively easy to use and calibrate.

From 1 January 2002, the exemption of using Freon for laboratory analytical purpose was running out. Unless one had applied to EU and got an approval, its use for offshore oil-in-water analysis has been prohibited.

For the purpose of reporting, it is understood that there are some variations between the different nations in the North Sea as shown in the Table 1.

Table 1 - Approved Oil-in-Water Analysis Method Currently in Use in The North Sea

Country	Denmark	The Netherlands	Norway	UK
OIW analysis methods currently permitted	IR+Freon Infracal HATR? GC-FID?	IR+Freon IR+Perklone	IR+Freon IR+Perklone? GC-FID	IR+Perklone

Perklone was officially approved by OSPAR in 1997 as a Freon replacement for the analysis of oil-in-water. As it has been suspected to be carcinogenic, the use of Perklone has been considered to be on a temporary basis. However there is no conclusive evidence to suggest that exposure to Perklone in the air is linked to human cancer. On the other hand all the studies conducted by offshore operators [5, 6, 7] have indicated that the Occupational Heath and Safety aspect for the use of Perklone can be controlled provided proper measures are taken.

Since the publication of the ISO 9377-2 method, the use of this ISO method for reporting purpose has been permitted by the Norwegian authority - the SFT. Norway is the only country at the present time to accept such a method for reporting. Norsk Hydro has already purchased a good number of GC-FID instruments that will be used offshore.

There are also other laboratory-based techniques, e.g. UV fluorescence based such as the Turner Design's TD-360 FastHEX and Arjay Engineering's FluoroCheck, and IR based Wilks Infracal HATR, that have been on trials in the North Sea. These methods are also simple, and easy to calibrate and use. However results from these trials are mixed with most cases trending well with the official approved infrared methods [7,8].

(b) On-line monitoring

There have been numerous trials of on-line oil-in-water monitoring systems in the North Sea [7, 9, 10]. To date successful applications have been few, also the applications have been limited to process control, other than reporting. There are a number of issues that may have hindered the successful applications of offshore on-line monitoring. These include:

- Variation in produced water characteristics

Produced water is in general a complex mixture. There are many parameters to consider when analysing its oil content in particular using on-line monitors. Such parameters may include free gas content, solid particles, dispersed and dissolved oil, oil droplet size and size distribution, ratio of the aromatic to the aliphatic hydrocarbons, presence of production chemicals such as corrosion inhibitors, demulsifiers, presence of methanol, temperature and salinity etc. Also all these parameters can be different from field to field, and may change from time to time.

- Sampling and sample handling

For both on-line monitoring and laboratory analysis, improper sampling and sample handling can cause a significant amount of errors to the measurement results. For on-line monitoring, there are a number of things that need to be looked at, which may include sampling point, sample probe design, sampling frequency, sampling velocity, sample conditioning etc.

- On-line monitor selection

Selection of an appropriate on-line monitor for a specific offshore application has never been an easy task. In order to select a proper monitor, one needs to understand clearly the application requirements, e.g. for regulatory compliance monitoring or process management. Also one needs to establish the sample stream characteristics and have a clear picture of

what techniques and instruments are available as well as their advantages and disadvantages.

- Calibration and maintenance

Long term accurate and reliable operation of on-line oil-in-water monitoring cannot be achieved without proper and regular calibrations and maintenance. There have been examples where an on-line instrument worked initially in a field and then its performance deteriorated, and eventually was 'abandoned' due to improper calibration and insufficient maintenance.

2.6 ISO 9377-2 GC-FID Based Method

The ISO method is based on an extraction of the water sample with a light hydrocarbon that has a boiling point between 36°C and 69°C, followed by a clear-up on florisil to remove the polar components, and then analysis using Gas Chromatography with Flame Ionization Detection (GC-FID) in the $C_{10}H_{24}$ (n-decane) to $C_{40}H_{82}$ (n-tetracontane) retention window. The concentration of the oil is quantified against an external standard consisting of two specified mineral oils.

The oil measured is therefore defined as "the sum of compounds extractable with a hydrocarbon compound, boiling point between 36°C and 69°C, not absorbed on Florisil and which may be chromatographed with retention window between $C_{10}H_{24}$ (n-decane) to $C_{40}H_{82}$ (n-tetracontane)" [1].

The method was established in response to the phase-out of Freon. As the method was developed with general oil-in-water analysis applications in mind, more importantly it was not developed for the analysis of volatile mineral oils. Thus, its suitability for offshore produced water oil content monitoring has been and is still questioned. A number of studies [4, 11, 12] have been carried out comparing the old IR based method and the ISO GC-FID or a modified version of the ISO GC-FID method using either field or simulated produced water samples. It is generally agreed that while the ISO method is robust, uses non-chlorofluorocarbon solvent, and proven, it does not seem to be practically suitable for offshore applications. Some of the major concerns of the ISO 9377 GC-FID method include

- Different definition of oil from Freon extraction and IR
- Require qualified and skilled personnel
- Measures carbon window from C_{10} to C_{40}
- Possible loss of hydrocarbons C_{10} above
- Requires new equipment
- Laborious and time consuming

OSPAR had clearly hoped to recommend the ISO GC-FID based method as a reference method for the determination of produced water dispersed oil. As the method was found to be inadequate for the determination of dispersed and total oil in the produced water derived from gas and condensate installations, modified methods have been proposed. These include [13]

(a) Still the original ISO GC-FID method, but specifically using pentane as an extractant, integrating the chromatograms from C_7 to C_{40}, and subtracting the TEX (Toluene, Ethyl-benzene and Xylene)
(b) Performing the original ISO GC-FID method in combination with static headspace or purge and trap to enable the analysis of C_5 to C_{10}. Again BETX (Benzene, Toluene, Ethyl-benzene and Xylene) are determined and subtracted from the integration.

Currently OSPAR is conducting a large programme aimed at comparing a modified ISO 9277-2 method as given in (a) above against the original IR method as specified by the OSPAR Agreement 1997-16. The programme has involved in taking a minimum of 4 replicate samples at each of 56 platforms distributed in the different parts of the OSPAR Maritime areas. The programme is led by the Netherlands with other participants including Denmark, Germany, Norway and UK [14].

The current state of the programme is that all results obtained have been sent to the Netherlands. The results are being statistically analysed by Dutch scientists and there will have a meeting in January 2003 to discuss these results. A final report will be prepared for the OSPAR OIC meeting in March 2003. A decision of whether or not to recommend this GC-FID based method for the determination of produced water oil content will be made then.

2.7 Measurement of Aromatics in Produced Water

Up untill recently the issue of aromatics in the produced water has largely been ignored from the regulation point of view. There have been no performance standards or reference methods agreed by OSPAR nations on aromatics in the produced water.

However it was made clear in the OSPAR Recommendation 2001/1[3] that OSPAR OIC should prepare for the Commission in 2003 a proposal for one or more performance standards, including appropriate reference analytical methods, and a timetable for the dates by which any such performance standards should be met.

To achieve this, a series of steps have been taken by the OSPAR. These include

- Exchange of information between the contracting parties by the year end of 2001 on methods of analysis of aromatics and actual data on aromatics
- Workshop event [13] in Netherlands to prepare sound advise on the analysis of aromatics
- Workshop [15] in Denmark to make final preparation on setting performance standards for aromatic hydrocarbons in produced water

Over the past few years, national authorities have asked offshore operators to analyse the aromatics, which are generally divided into BETX, NPD (Naphthalene, phenanthrene, dibenzothiophene) and PAHs (polycyclic aromatic hydrocarbons represented by 16 EPA PAHs). However frequency of these analysis varies from nation to nation. In Norway and UK, for an example, most installations were asked to have one analysis per year, while in the Netherlands a sampling and analysis frequency of 1 to 5 times a year have been agreed depending on the amount of discharge per platform [16].

Table 2 shows average concentrations of the different aromatic groups specified for gas, oil and oil/gas production in the North Sea. The average concentrations were calculated based on analyses for 16 EPA PAHs, sum of BTEX, and NPDs respectively from 209, 212 and 28 platforms in the North Sea [16].

Table 2 Average Concentrations Of The Different Aromatic Groups In The Produced Water [16]

	Gas (µg/l)	Oil (µg/l)	Oil/Gas (µg/l)
Sum 16 EPA	346	222	442
Sum BETX	135728	10499	15694
Sum NPD	1103	856	2086

However it is not all clear how the samples were taken and what exactly the analysis methods were used in obtaining the concentration of the various aromatics.

3 WHERE ARE WE HEADING IN OFFSHORE OIL-IN-WATER MONITORING?

The issue of oil-in-water monitoring offshore is ultimately driven by the legislation and it is expected that more stringent regulations will be introduced.

3.1 Aromatics in Produced Water

As mentioned in the earlier sections, OSPAR is currently working on the issue of the discharge of aromatic hydrocarbons. It is expected at the OSPAR OIC meeting in March 2003

that there will have a proposal prepared for performance standard(s) on aromatics in produced water.

At the recent OSPAR workshop event held on 27-28 November 2002 in Denmark[15], the need for performance standards as well as the feasibility of compliance to such performance standards were extensively discussed. In order to establish whether there is a need for performance standards, information on background aromatics in sea water, actual concentration and load of aromatics discharged by offshore installations, information on hazard profiles and risk analysis were presented and discussed. The conclusion from the extensive discussion seems that with the current available data no reason can be found to justify the definition of a performance standard for a specific aromatic hydrocarbon.

On the issue of feasibility of compliance, information on both available aromatics reduction techniques and available analysis techniques were presented and discussed. Two reduction techniques were identified, both of them are of extraction types. These techniques were considered to be technically possible to significantly reduce the amount of aromatics under certain circumstances. On the analysis methods, it is recognised that the use of a single method for the determination of all the groups of aromatics is not possible. However, well established methods are considered to be readily available for all three groups of aromatics though samples may have to be sent to land based laboratories. The selected analysis methods include

- BETX: Head space with GC-MS or GC-FID, liquid extraction and GC-MS
- PAHs and NPDs: liquid extraction and GC-MS

Overall the case for establishing performance standards on aromatics is not as strong as it first appears. However this does not mean there will have no action on the issue of aromatics. From the information gathered, there will seem to set platform specific performance standards based on risk assessment and OSPAR principle of BAT (Best Available Technology) and BEP (Best Environment Practice) in the future. Details will be clear in March 2003 at the OSPAR OIC meeting.

3.2 Dispersed oil in produced water

(a) Reference Methods For The Determination Of Dispersed Oils

Before any new method is recommended, the official approved method as given in the PARCOM Agreement 1997-16 will remain. All the evidence shows that Perklone is a good Freon replacement from an IR analysis point of view as results obtained using IR/Perklone are comparable to those from using IR/Freon [4, 12]. This is the case both for black oil and gas condensate oil in water. Also provided adequate measures are taken, the issue of Occupational Health and Safety is clearly controllable from the recent operator studies [5, 7]. In addition it has been reported that Perklone has a negligible photochemical reactivity [17], i.e. not an ozone depleting substance as may have been suggested previously.

Using Perklone as a Freon replacement in the IR analysis has the following key advantages

- Using the same IR method
- Legislation continuation and easy interpretation of historical data
- No change of equipment and easy operation

However it has been clear that OSPAR intends to recommend a GC-FID based method for the determination of the dispersed oil in offshore produced water. OSPAR hopes that the current comparison programme, which involves analysing samples taken from 56 platforms in the North Sea, will enable it to recommend such a method next year.

It looks increasingly likely that a new reference method for the dispersed oil determination will be a modified version of the original ISO 9377-2 GC-FID. The modified method will involve using pentane as an extractant, and integrating from C_7 to C_{40}, and then subtracting the TEX (Toluene, Ethyl-benzene and Xylene) to obtain the dispersed oil. Available results indicated

that such a method would approximate the dispersed oil to the IR method better than the original ISO method, but still there are significant differences as data in the Table 3 shows,

Table 3 - Difference of Dispersed Oil Measured By The Modified Method and Old IR Method [14]

Installation types	OSPAR Freon based IR method (mg/l)	Modified ISO GC-FID method (mg/l)	Percentage difference based on IR results (%)
Gas condensate 1	30	22	-27
Gas condensate 2	60	58	-3
Gas condensate 3	30	27	-10
Light oil	23	22	-4
Oil 1	8	5	-38
Oil 2	34	23	-32

In addition the modified method would bring the following further disadvantages:

- Not as robust as the original ISO method
- Requires higher resolution gas chromatography instruments

More importantly available data as given in Table 4 [14] showed that there were considerable differences between the total oil as measured by the modified method and that by the old IR method, in particular when samples from gas and condensate installations were analysed.

Table 4 - Difference of Total Oil Measured By The Modified Method and Old IR Method [14]

Installation types	OSPAR Freon based IR method (mg/l)	Modified ISO GC-FID method (mg/l)	Percentage difference based on IR results (%)
Gas condensate 1	864	61	-93
Gas condensate 2	125	70	-44
Gas condensate 3	144	45	-68
Light oil	27	26	-4
Oil 1	9	6	-33
Oil 2	39	24	-38

With available data from the latest Netherlands' study [12, 14] and those obtained from OLF and UKOOA [4, 11] questions must be asked with regard to the suitability of a GC-FID based method for the determination of offshore produced water oil content.

If such a method is still to be recommended next year, what will happen with regard to the performance standard? There may be two possible options

- Keep the current performance standard and establish a correlation between the two methods
- Redefine the performance standard by OSPAR

Whatever the case, all other methods (laboratory based and on-line monitoring) will then have to be calibrated against this new method. With lack of field GC-FID instruments specifically designed for offshore produced water oil content analysis, and also lack of skilled GC-FID operators togather with a rather complex method, there may be considerable difficulties to be faced by the offshore operators in the implementation of the method.

(b) Bench Top Based Techniques Available For Routine Offshore Monitoring

Regardless of whether or not a GC-FID based method will be recommended by the OSPAR next year, methods that are relatively easy to calibrate and operate, and can be used for routine offshore oil-in-water analysis uses, are always useful. In the case where a GC-FID

method is recommended, alternative methods for routine oil-in-water monitoring will be needed.

As mentioned earlier there are a number of laboratory-based techniques, e.g. UV fluorescence and Wilks Infracal HATR, that have been on trial in the North Sea. These techniques do not necessarily require the use of chlorofluorocarbon solvent. Also the search for new Freon/Perklone replacements that are safe and more environmentally friendly continues, in particular in the USA [18]. In addition studies have also been carried out where a solvent that contains C-H bond has been investigated for the suitability of infrared oil-in-water analysis [19].

It must be pointed out that different methods will measure oil differently. For example, UV based instruments measure the intensity of fluorescence that occurs after oils containing aromatics are irradiated using UV light. Therefore these instruments respond to the aromatics. Oil concentration can only be calculated with a calibration and the ratio of aromatic to the aliphatic (or total) hydrocarbons must remain relatively constant. Also it should be pointed out that each method will have its limitation and a detection range that may not be the same as the old IR or the ISO GC-FID method. The most important thing is to ensure that there is a valid calibration against the reference method(s) over the concentration range of interest.

As well fluids from different reservoirs and fields are increasingly co-mingled and processed via a central platform/installation, even with the old IR method, there would have been problems in keeping the calibration curve up to date. In the cases where well fluids from oil fields and gas condensate fields are co-mingled, the situation can be worse for a GC-FID based than the old IR based method as the IR based method tends to be less sensitive to a change of the aromatic content.

It is likely that there will have to be a range of instruments using different detection principles for offshore routine monitoring applications. Each of them will be calibrated for a specific offshore application. This will be in strong contrast to previous situation where IR methods were used throughout. Table 5 provides a list of available bench top techniques that may be used for offshore routine oil-in-water measurements.

Table 5 - List of Bench Top Techniques For Routine Oil-In-Water Monitoring

Technique	Principle and Applications
IR + alternative C-H bond free solvents	Exactly the same as IR/Freon or TTCE method but using alternative C-H bond free solvents such as Horiba S-316 [20]. Applicable to both oil and gas condensate installations
Wilks Infracal HATR	Infrared absorption takes place by penetrating IR beam into a thin oil film left after the evaporation of the extraction solvent. Not suitable for gas condensate installations.
UV fluorescence	Measure aromatic hydrocarbons. When the ratio of aromatic to aliphatic hydrocarbons remain constant, the aliphatic or total oil can be calculated. Only suitable where the ratio of aromatic to aliphatic can stay relatively constant.

(c) On-line Oil-in-Water Monitoring

With Freon being phased-out, other alternative bench top methods have yet been firmly established. Also there is an increasing drive to optimize produced water treatment process with an ever increasing amount of water produced. On-line monitoring has been increasingly looked on by both offshore operators and regulatory bodies as a method for the future.

On-line oil-in-water monitoring has been a subject of interest for many years, e.g. in 1983/84 the then E&P Forum conducted a questionnaire survey [21] investigating operators' experience in using on-line oil-in-water monitors. Also in the 1990's there were a number of Joint Industry Projects [22-25] aimed at identifying a suitable on-line oil-in-water monitor for the use of offshore. Furthermore there have been new developments in the technology as

well as improvements made to old technology. Yet few successful applications exist in the North Sea. We have to ask ourselves as to why there have been so few success stories and what each of us (monitor suppliers, regulators and offshore operators and contractors) can do to improve and to make on-line oil-in-water monitoring a reality.

There are a number of things that we believe we should do:

(a) Detailed specifications from regulatory bodies

On-line oil-in-water monitoring is accepted by the OSPAR as an alternative method for reporting provided that they are calibrated against the reference method and yield equivalent results. However there is nothing detailed on how a calibration should be carried out and what is considered to be "yielding equivalent results". It should be certainly helpful to both the on-line monitor suppliers and offshore operators if the following can be clearly specified or there are guidance notes available from regulatory bodies.

- (Realistic) acceptable accuracy?
- (Realistic) acceptable instrument operation availability?
- Calibration routine and number of calibrations?
- In a situation where on-line monitor fails, what should the operator do?
- Are manual samples still required to be analysed while on-line monitor is in operation? If so, when and how many?
- What data should be reported and how should they be reported?

(b) Development of best practice guidelines

As mentioned earlier there are a number of issues that may have hindered the successful application of offshore on-line monitoring. These issues range from variation of the produced water characteristics, monitor selection, installation, sampling and sample pretreatment to calibration & maintenance and operator training. Despite the fact that there have been few successful on-line oil-in-water monitoring experiences, there is a plenty of useful experience obtained from testing and trials of on-line oil-in-water monitors that one can draw on to establish such best practice guidelines. Also useful experience gained from other industries that use on-line monitoring instruments for process control should be referenced.

(c) Emphasis on field testing

Testing of on-line oil-in-water monitors in a laboratory environment is certainly useful both for instrument development and works testing. However produced water is complex in nature, it is therefore extremely difficult to simulate and reproduce in a laboratory environment.

(d) Super Fluid Extraction and Infrared (SFE-IR)

A new method has been recently developed based on using supercritical CO_2 fluid extraction and Infrared quantification [26]. The method is essentially the same as the old IR method, but instead of using Freon or Perklone to extract the oil from water samples, it uses liquid carbon dioxide. Though the method was primarily developed for the analysis of mineral oil in water samples derived from land based industries, it has significant potential to become a method both as a reference method and a method for analysing field samples from offshore.

Unlike the ISO 9377 GC-FID method, volatile mineral oils can be analysed using the method. Also depending upon the IR instruments used, both aliphatic and aromatic hydrocarbons can be analysed. Details of the technology is presented elsewhere at the seminar. It is also anticipated that an independent evaluation testing programme will be launched to compare the SFE-IR method to the current IR + Perklone method, using simulated produced water samples and/or real samples from offshore [27].

4 CONCLUSIONS

- The approved IR+Perklone based oil-in-water analysis method is still valid and considered to be the best practical solution for offshore oil-in-water monitoring.

- The ISO 9377-2 GC-FID method was never developed for the determination of volatile mineral oils. Therefore unless OSPAR was prepared to recommend two methods – one for oil installations and one for gas condensate installations, its suitability as a reference method for offshore produced water oil content analysis should have been questioned at the very beginning.

- A modified ISO GC-FID 9377-2 method, that uses pentane as an extractant, integrates the chromatograms from C_7 to C_{40} and subtracts the TEX (Toluene, ethyl-benzene and xylene) to obtain the dispersed oil content. This may provide a better approximation for the dispersed oil to the old PARCOM method. From current available data the question of the suitability of such a method for the determination of offshore produced water oil content remains.

- A number of bench top techniques are available. They are potentially suitable for the routine monitoring of oil content in the produced water. Due to the considerable variations in the characteristics of produced water, and the limitation of each of these bench top techniques, it is likely that we will see a range of instruments for offshore routine monitoring applications.

- A new oil-in-water analysis method that is based on supercritical carbon dioxide fluid extraction and IR quantification has been developed. The method is considered to have significant potential for becoming a reference method and a method that may be used for analysing field samples from offshore.

- On-line monitoring will be increasingly looked on. However the key to success will not only depend upon further development of more reliable and accurate instruments but also perhaps more importantly on how we use them in the field. Better specifications from regulators, the development and uses of best practice guidelines, and collective field testing will all be needed.

- On the issue of aromatics in produced water work has been carried out by OSPAR aiming to propose performance standards and reference analysis methods. However it is unlikely that specific discharge levels will be set on the various aromatic groups across board, instead platform specific performance standards based on risk assessment and OSPAR principle of BAT and BEP will probably be set.

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