Development of an analytical method suitable for on-site measurement of thermodynamic hydrate inhibitors in oilfield produced fluids

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Introduction

Methanol and monoethylene glycol (MEG) are thermodynamic hydrate inhibitors used to prevent the formation of gas hydrates in oil and gas pipelines. Gas hydrates are ice-like solids with gases, such as methane, trapped inside crystalline water cages. Hydrates can block pipelines and remediation is often costly and potentially dangerous; if hydrate formation is considered to be a risk it is essential that a prevention or management strategy is implemented. The stability of the hydrate structure means they are capable of forming at temperatures well above the melting point of water. Systems are particularly at risk of hydrate formation during well start-up, during shut-ins or when operating at a low flow rate [1]. Thermodynamic hydrate inhibitors effect their action by altering the chemical potential of the aqueous phase (by interfering with intermolecular interactions) and consequently displacing the equilibrium dissociation curve to lower temperatures and higher pressures. The chemical potential of the water molecules is decreased and the equilibrium in the following reaction shifts to the left [2].

$$\text{Water} + \text{Gas} \rightleftharpoons \text{Gas Hydrate}$$

The choice between methanol and MEG often comes down to cost and while methanol is less expensive than MEG it is more difficult to reclaim, therefore if continuous injection of hydrate inhibitor is required (for example to protect a long tie-back) then MEG is generally chosen [3].

Methanol and MEG concentrations are monitored for fiscal purposes; their presence in hydrocarbon fluids reduces the quality and therefore the value of such products. They cause problems during processing and refining, such as separation difficulties, poisoning catalysts and poisoning molecular sieve beds and as a consequence refineries and terminals often impose limits on the acceptable level of hydrate inhibitor where exceeding these limits can incur large fines [4,5]. Operators can therefore be faced with the decision to either defer start-up and lose production revenues or start-up and risk a charge. Monitoring the concentration of methanol and MEG in produced water can also be important to ensure compliance with environmental regulations, while checking levels in the water streams of reclamation / regeneration facilities helps ensure equipment is working as effectively as possible.

Gas chromatography (GC) is the traditional method for monitoring methanol and MEG in produced fluids, however this technique has a number of drawbacks, particularly when used in an offshore environment. Gas chromatographs are sensitive pieces of equipment and can suffer from maintenance issues, they can also be complex to run and therefore require experienced personnel. Preparing samples for analysis often involves a water separation step where the inhibitor is transferred from the oil phase into the aqueous phase, this can be time consuming and is

subject to user variation. Shipping samples to shore is an option, however while operators are awaiting results there is the risk of a production issue occurring that could potentially have been mitigated by analysis of the sample the day it was taken. Shipping samples also introduces additional uncertainty in the results, as samples may change with time. Ideally operators would be able to analyse hydrate inhibitors such as methanol and MEG on-site so they could respond more promptly to the information.

The development of a simple, easy to perform analytical method that uses robust equipment would overcome many of the issues encountered with gas chromatography and would be of particular benefit for use offshore or in remote locations where shipping of samples to an onshore laboratory is not practical. This paper describes a colorimetric method, called OMMICA™, for monitoring the concentration of thermodynamic hydrate inhibitors, methanol and MEG, in produced fluids, and includes results which demonstrate the specificity and sensitivity of the method. Data from offshore field trials showing OMMICA™ can be used in these environments and deliver reliable results is also presented.

Method

Materials and Equipment

OMMICA™ kits were used to determine methanol and MEG concentrations in produced fluids. Three different types of kit were used for this work – methanol, MEG in water and MEG in oil. Each kit contains borosilicate glass tubes and Reagents to run a standard curve, blank controls and samples. Analytical grade methanol, MEG, ethanol and diochloromethane (DCM) were purchased from Fisher Scientific and deionised water was used throughout. A specially adapted rotating heater designed to hold twelve 16 mm tubes was used to heat and mix samples. The centrifuge, heat block and spectrophotometer were also designed to take 16 mm tubes. Positive displacement pipettes were used to accurately measure oil and solvents, while air displacement pipettes were used for aqueous solutions, such as water samples and reagents.

OMMICA™ Protocol

Methanol detection: five methanol standards were analysed to create a standard curve; each methanol standard solution (2.5 ml) and a portion of reagents (7.5 ml) were placed in five separate glass tubes. Each tube was placed in a rotating heater designed to rotate tubes end over end for 35 min, the temperature was set to 50°C. The absorbance of each sample was then recorded (Figure 1). For detection of methanol in water, the aqueous (2.5 ml) sample was mixed with reagents (7.5 ml) and the procedure described above followed. Some interference can result from high levels of salt and for high-salt samples a 10-fold sample dilution step was incorporated.

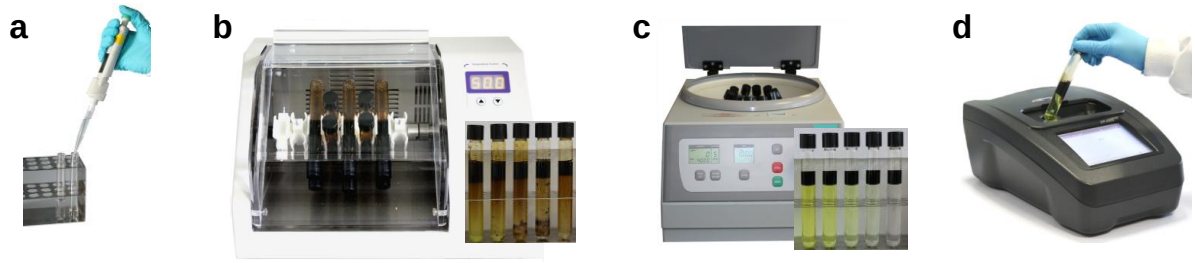

Figure 1: OMMICA™ method, a) add reagents and sample to tube, b) heat and rotate, c) centrifuge (for oil samples) to separate aqueous and hydrocarbon layers and d) analyse in spectrophotometer.

For oil samples, deionised water (2.5 ml) and reagents (7.5 ml) were placed in each tube, then 1 ml oil / condensate added using a positive displacement pipette. The tubes were shaken briefly to mix. Smaller or larger volumes of oil can be used depending on the methanol concentration. After heating, the tubes were centrifuged to separate the two phases and then the absorbance recorded. To account for any interferences or coloured components which may be present, particularly in heavier crude oils, a sample called a blank was also run and the absorbance subtracted from the actual sample absorbance. The concentration of methanol in oil samples was then calculated from the standard curve.

Note, while the use of the adapted heater / rotator is described for the above methods, this piece of equipment is only required for oil samples as it the rotating action that mixes the two phases and extracts the methanol or MEG into the aqueous phase for detection. For water only samples, this piece of equipment can be substituted for a heat block and the centrifuge step is no longer necessary (Figure 2).

Figure 2: OMMICA™ method for water samples, a) add reagents and sample to tube, b) heat and c) analyse in spectrophotometer.

MEG detection: MEG standard solutions (0.5 ml) and Reagent A (2 ml) were placed in five separate glass tubes. After heating for 15 min, Reagent B (2.5 ml) was added and the tubes heated for a further 30 min. The absorbance of each tube was then recorded. To measure MEG water samples the procedure above was repeated with 0.5 ml sample added in place of MEG standard solution. For oil samples, deionised water (0.5 ml) and Reagent A (2 ml) were added to a tube followed by 1 ml of oil / condensate. After a brief shake to mix, the tubes were heated and rotated for 15 min, then Reagent B (2.5 ml) added and the tubes heated for a further 30 min. After heating, the tubes were centrifuged to separate the two phases and then the absorbance recorded.

Methanol was spiked into oil, using dichloromethane (DCM) as a co-solvent, at final concentrations in oil of 0, 7.8, 15.6, 31.3, 62.5, 125, 250, 375 and 500 parts per million (ppm). Different volumes of oil were used in the method to focus the assay in different ranges (0.25 ml for 0 – 500 ppm; 3 ml for 0 – 30 ppm).

The amount of methanol extracted from the oil phase using different methods was compared. This was to better understand the potential effects manual extraction by different users may have and what benefit may be offered by an automated extraction step. Running OMMICA™ directly on an oil sample was compared to a vigorous manual extraction, a gentle manual extraction and a heated / automated extraction (Table 1).

Table 1: Description of conditions used to compare different water extraction methods to OMMICA™.

	Method	**Method description**	**Replicates**
1	OMMICA™	2 ml oil plus 10 ml reagents run using standard OMMICA™ method for oil	3 separate tubes
2	Vigorous manual extraction	Water and oil (15 ml of each) placed in separating funnel, shaken vigorously for 2 min then water phase separated and analysed by OMMICA™ methanol in water method	1 extraction → water phase spilt into 3 x 2.5 ml for OMMICA™ analysis
3	Gentle manual extraction	As above, except shaken gently for 2 min	As above
4	Heated / rotated automated extraction	2 ml oil plus 10 ml water, heated and rotated for 35 min (to mimic OMMICA™ method). Water phase separated and 2.5 ml analysed by OMMICA™ methanol in water method	3 extractions, each analysed once by OMMICA™

The same experiment was repeated with MEG with slightly different volumes to match the MEG protocol.

A series of methanol in water solutions (0, 1, 2, 5, 10, 20, 50, 100, 200 and 500 ppm) was prepared and analysed by OMMICA™ and GC, each solution was run in duplicate. The measured methanol concentration in each sample was calculated from a set of standards previously analysed using both methods.

The specificity of the methanol assay for methanol was investigated by spiking samples containing methanol with 25 ppm ethanol and MEG. The assay for MEG was tested for interference from methanol and ethanol by spiking samples containing MEG with 25 ppm of each alcohol.

<u>Methanol in Produced Water Field Trial</u>

The methanol trial was conducted on the Scott platform owned by Nexen Inc. and situated in the North Sea. Methanol was injected at a flow rate of 3.2 m^3/hr for 160 min. As soon as the methanol pump was switched on sample collection began at the second and third stage separators. Water samples were collected every 15 min for 4

h, then every hour up to 12 h. An initial trial was conducted with the typical well set-up, then a second trial was conducted which involved the introduction of a high water well. Only samples from the third stage separator are discussed in this paper as many of the second stage samples were >10,000 ppm. For the first trial, each of the 25 samples were analysed by OMMICA™ and gas chromatography; for the second trial only every second sample was analysed by OMMICA™. The samples were shipped onshore for GC analysis, the delay between running OMMICA™ on the platform and running the GC was more than 6 weeks.

MEG in Water Field Trial

Water samples were collected from various sampling points on a MEG regeneration facility. These were analysed on the same day as collected, by both OMMICA™ and GC.

Results and Discussion

OMMICA™ - Methanol Method

OMMICA™ was tested by adding known amounts of methanol to oil. Up to 500 ppm methanol can be detected (Figure 3); sensitivity at lower concentrations can be improved by increasing the volume of oil used in the assay and quantification down to 2 ppm is possible. The results clearly show the method works well with oil samples.

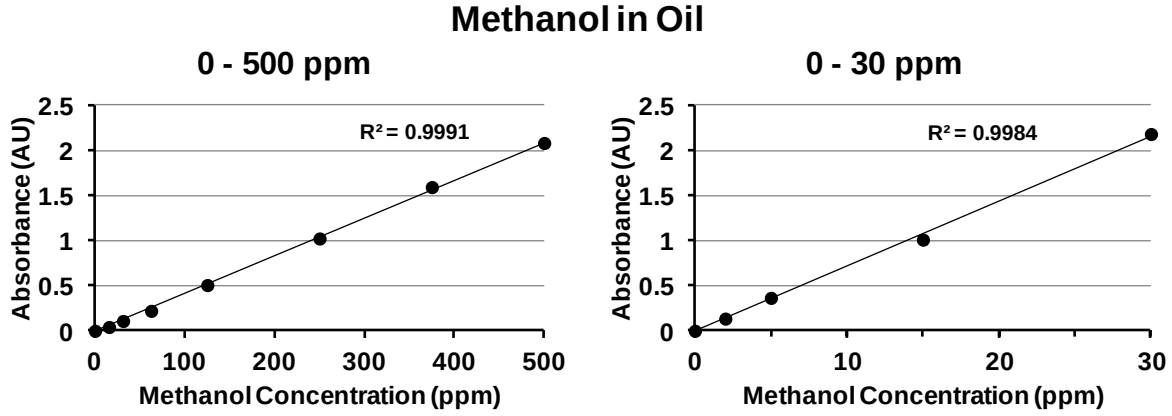

Figure 3: Relationship between methanol concentration (ppm) and absorbance (absorbance units) of samples analysed using the methanol detection method. Data fitted linearly with $R^2 > 0.99$.

The traditional method for monitoring methanol concentration in oil is by gas chromatography (GC). This can be run on the oil sample directly or on a water extract. ASTM method D7059 [6] involves dilution of an aliquot of oil with toluene, followed by direct injection of the hydrocarbon mix into the GC. This ASTM method is commonly used in the United States however it is less widely used in other regions and indeed during the OMMICA™ validation work it was difficult to find a company in the UK with the capabilities to run this method because of the multidimensional GC set-up required. The method that seems to be more commonly used in the North Sea region involves a water extraction, where a portion of water is mixed with the oil sample and the majority of the methanol present preferentially passes from the oil phase into the aqueous phase. The water sample is then analysed for methanol content by GC. This approach was used through the work reported here. However, we note that this water extraction and separation step can be onerous and opens up

the technique to user variability - different operators may use different amounts of water, and shaking time and level of vigour may not be uniform.

To investigate this further and determine the likely impact of user variation, an experiment was conducted to investigate the amounts of methanol extracted from oil by four different methods:

1) OMMICA™ - oil and aqueous reagents mixed and reacted
2) Manual water extraction and separation (shaken vigorously)
3) Manual water extraction and separation (shaken gently)
4) Automated water extraction (heated / rotated)

Water extract analysed by OMMICA™

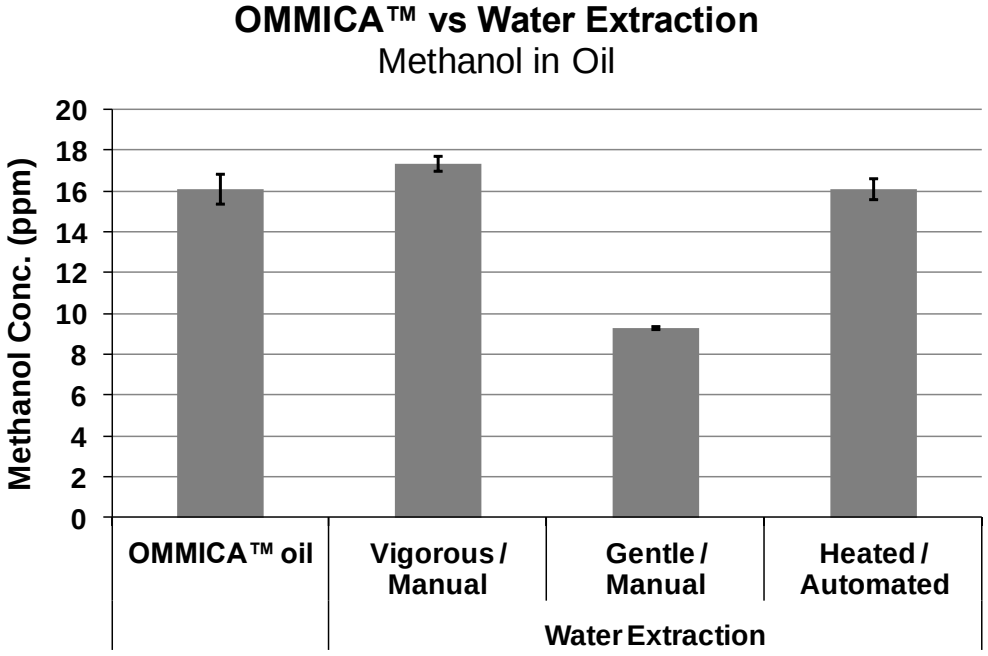

Figure 4: Oil sample run directly using OMMICA™ method compared to manual and automated water extraction. Results are the average of triplicate samples and error bars represent standard deviation.

The results in Figure 4 show a much lower (*ca.* 50% lower) amount of methanol present in a water sample where the methanol has been extracted from oil by gentle shaking, compared to the three other methods tested. This highlights the importance of having a reproducible extraction method. This result gives us confidence that the automated method used for OMMICA™ is extracting the same amount of methanol as a vigorous manual extraction, but in an approach that will be more consistent.

It is also important to show that OMMICA™ and GC detect the same levels of methanol. Figure 5 shows a comparison between OMMICA™ and GC over a 0 – 500 ppm range in aqueous samples, with the data giving an excellent match.

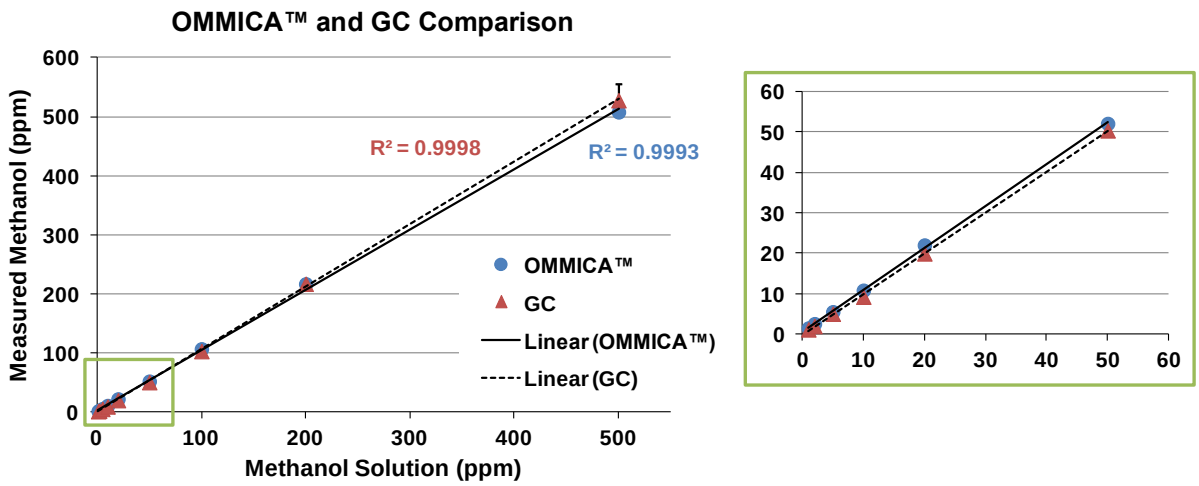

Figure 5: Comparison of OMMICA™ and GC results from analysis of aqueous samples containing methanol (0 – 500 ppm). Data represents average of duplicate samples and error bars are standard deviation.

Results from testing the specificity of the OMMICA™ method demonstrate that the methanol detection method is highly specific for methanol and no signal from ethanol or MEG is observed (Figure 6).

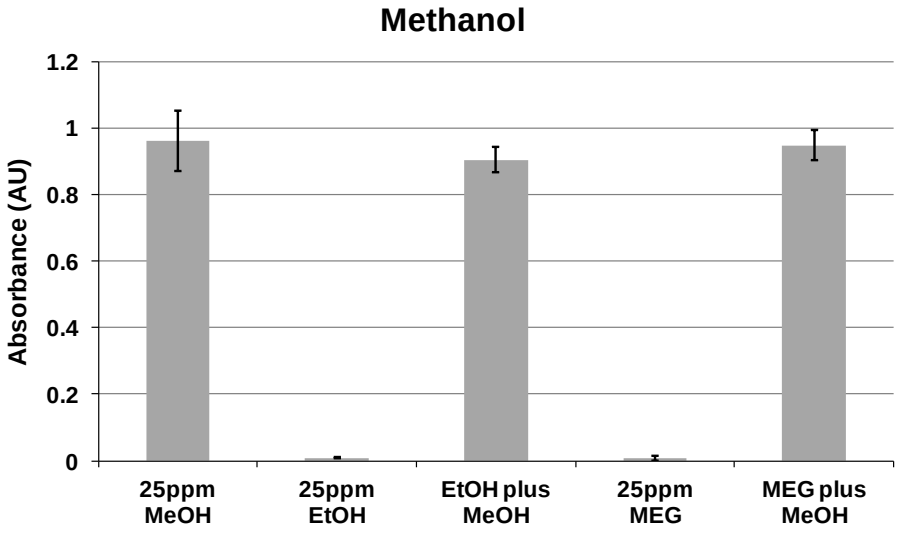

Figure 6: Effect of chemically similar molecules, ethanol and MEG, on signal produced by the methanol detection method.

OMMICA™ - MEG Detection

Figure 7 shows the relationship between MEG concentration in water and absorbance as determined by the MEG detection method. The graph covers the 0 – 100 ppm range but can easily be expanded by simply pre-diluting the samples in water.

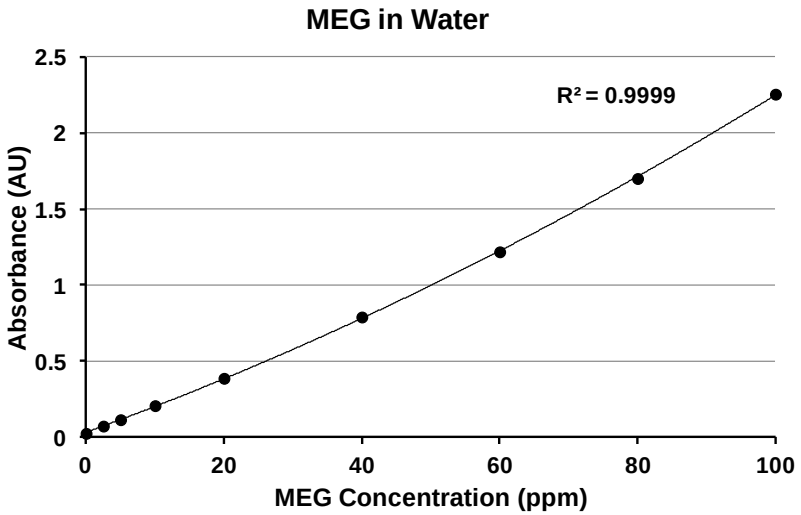

Figure 7: Relationship between MEG concentration (ppm) and absorbance (absorbance units) of samples analysed using the MEG detection method. Polynomial fit applied to data with R^2 = 0.9999.

The method was also shown to work well in oil. Figure 8 shows the relationship between signal and concentration of MEG in crude oil. The range of the assay can be changed by altering the volume of oil added; using a volume of 3 ml allows greater accuracy in the low ppm region while decreasing the oil volume to < 1 ml extends the range to at least 500 ppm.

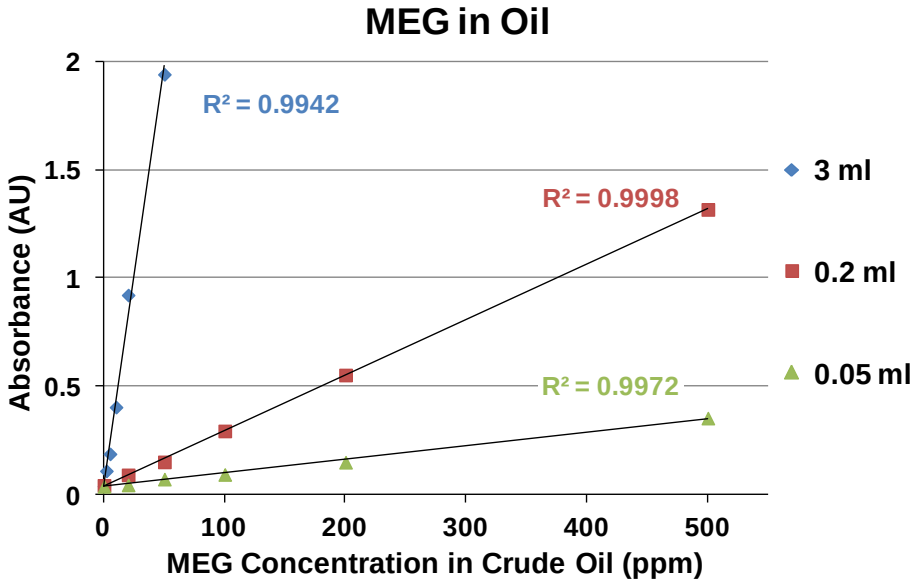

Figure 8. Analysing MEG in crude oil using different volumes of oil to alter the range of the method.

The MEG results from the comparison of OMMICA™ and different extraction methods were very similar to those for methanol. OMMICA™, vigorous manual extraction and the heated / automated extraction results all matched well, while the MEG concentration detected in the aqueous phase after a gentle manual extraction was significantly lower (Figure 9).

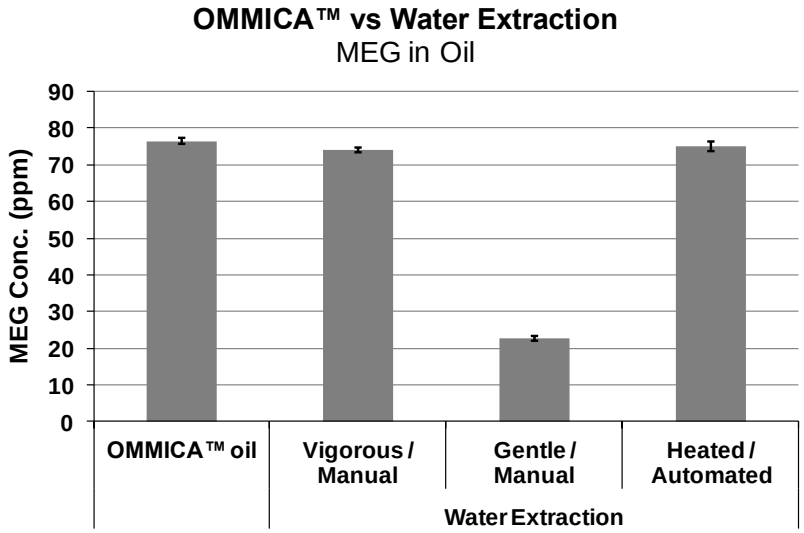

Figure 9: Oil sample run directly using OMMICA™ method compared to manual and automated water extraction. Results are average of triplicate samples and error bars represent standard deviation.

The MEG detection method is highly specific for MEG and no signal from methanol or ethanol is observed. Furthermore, the presence of these alcohols does not interfere with the MEG signal (Figure 10).

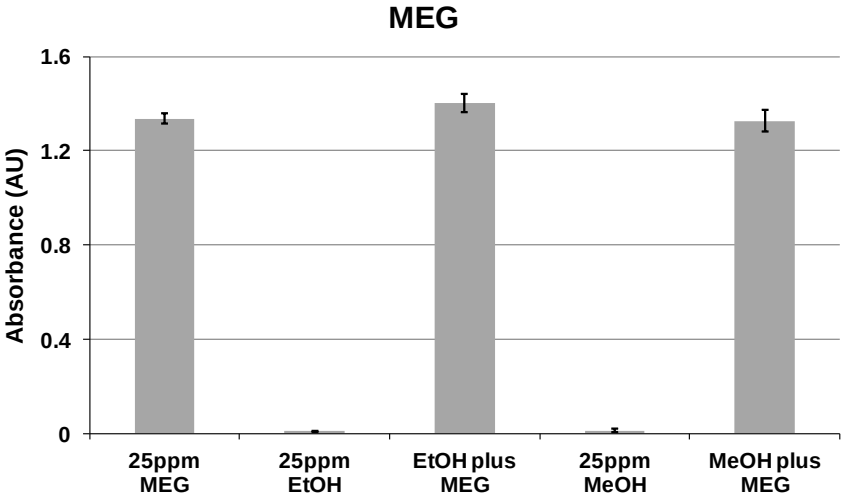

Figure 10: Effect of chemically similar molecules, methanol and ethanol, on the MEG detection method.

OMMICA™ has been previously used successfully offshore [7], here we report data from field trials where the results from the methanol and MEG detection methods are compared to GC results.

Methanol in Produced Water Field Trial

A methanol in produced water field trial was carried out on the Scott platform in the North Sea. Methanol was injected for 160 min and water samples collected for 12 h from the time the methanol pump was turned on. Frequent sampling (every 15 min) was employed at the start which then decreased to hourly sampling after 4 h. The

samples were analysed using the OMMICA™ methanol detection method very soon (hours) after collection. This quick turnaround means onsite personnel can be immediately aware of how much methanol is coming through the system and also allows methanol transit time to be accurately calculated while still relevant.

The correlation between OMMICA™ and GC results was excellent. The methanol peak appeared at the same point in both sets of data (Figure 11) and the overall trends matched well. The methanol concentrations calculated by GC are lower than those calculated by OMMICA™; this is believed to be due to the large time delay (> 6 weeks) between the two sets of analyses. This emphasises the benefit of analysing samples offshore or onsite as soon as possible after collection to accurately determine methanol concentrations. Overall, the amount of methanol detected during trial 2 was lower, this was caused by the introduction of a high water well which diluted the samples.

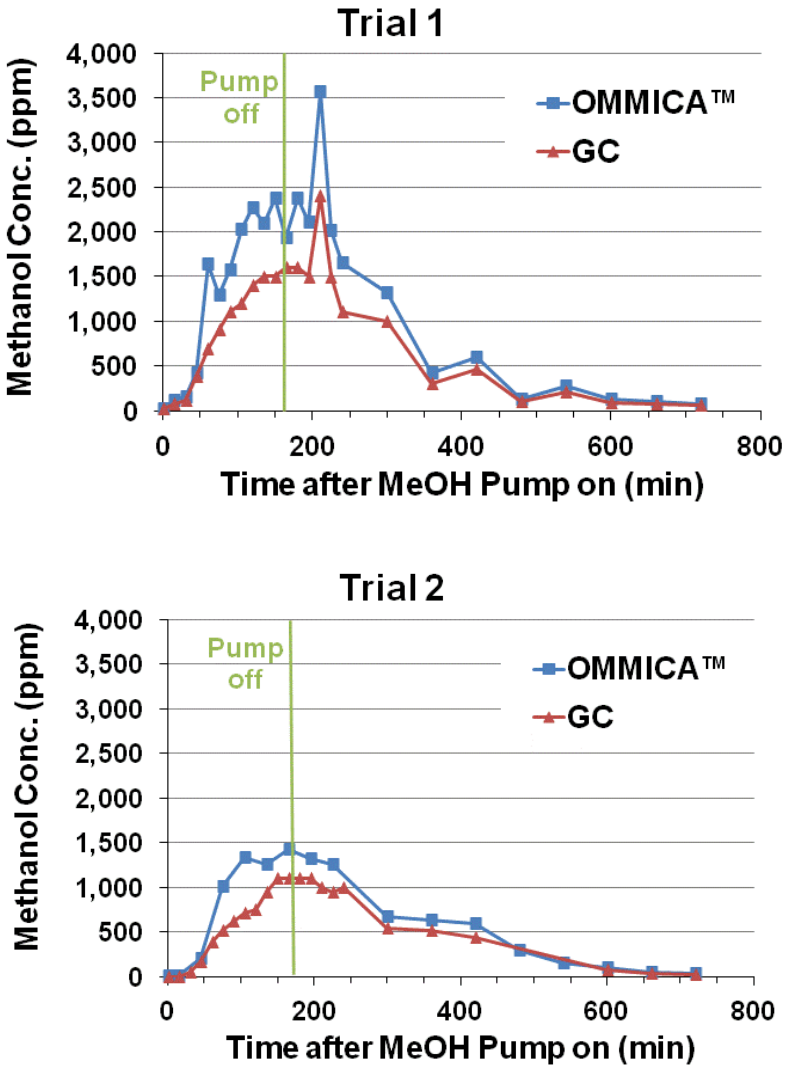

Figure 11: Methanol concentration in produced water samples as determined by OMMICA™ (offshore) and GC (onshore, >6 weeks later).

The methanol concentrations calculated by GC were roughly 70% of the OMMICA™ results. Applying a factor of 70% to the OMMICA™ results produces data which overlays the GC data well (Figure 12).

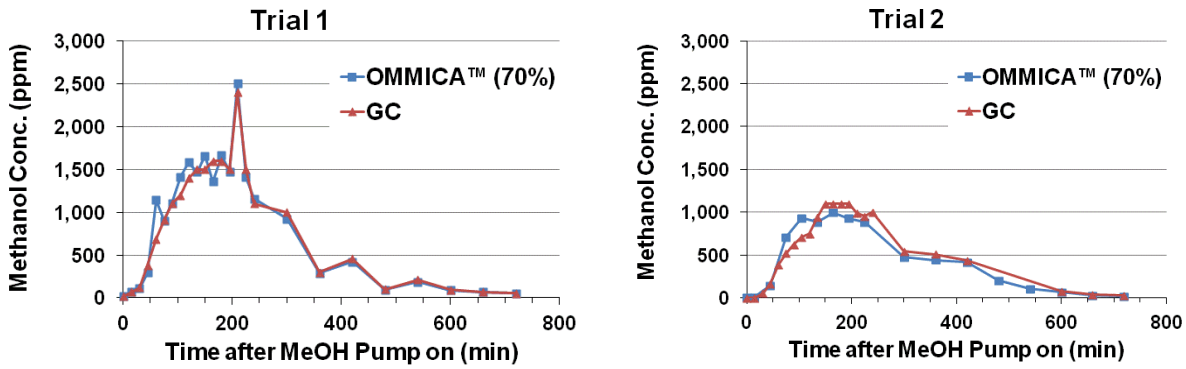

Figure 12: Methanol concentration in produced water samples as determined by OMMICA™ and GC. A 70% factor has been applied to the OMMICA™ results.

The decrease in methanol concentration with time has been observed before. A previous offshore trial on a different asset in the North Sea involved analysing oil samples on three separate occasions.

Figure 13 shows that the level of methanol in almost all samples decreases with increasing length of time after collection.

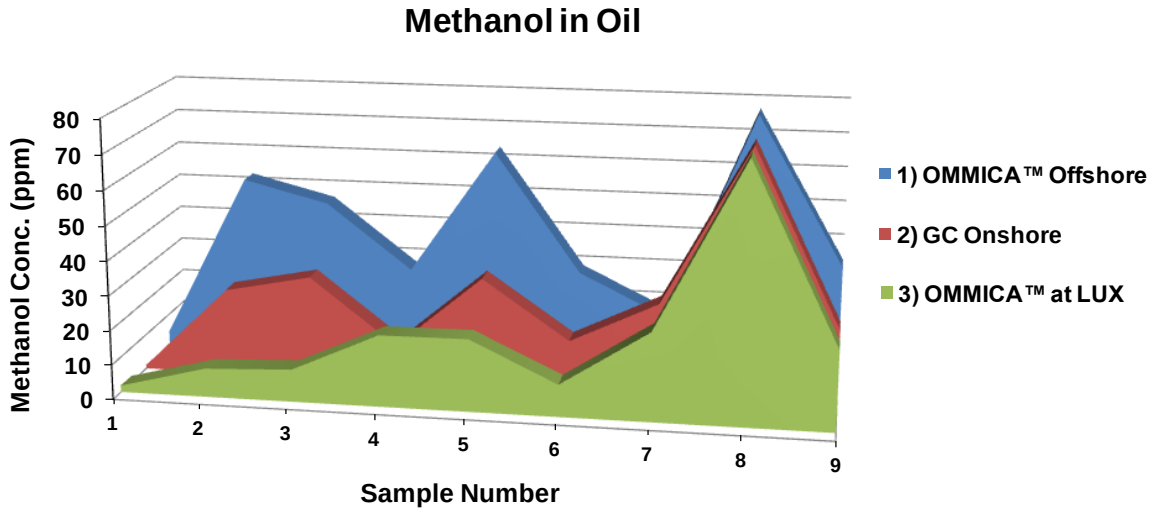

Figure 13: Methanol in oil detection using both OMMICA™ and GC at various times after samples collection.

MEG in Water Field Trial

The OMMICA™ MEG in water kit was used by an oil and gas operator with a MEG regeneration facility, to analyse samples containing MEG. For comparison purposes the samples were also analysed by GC. As can be seen in Figure 14 the two methods correlate extremely well.

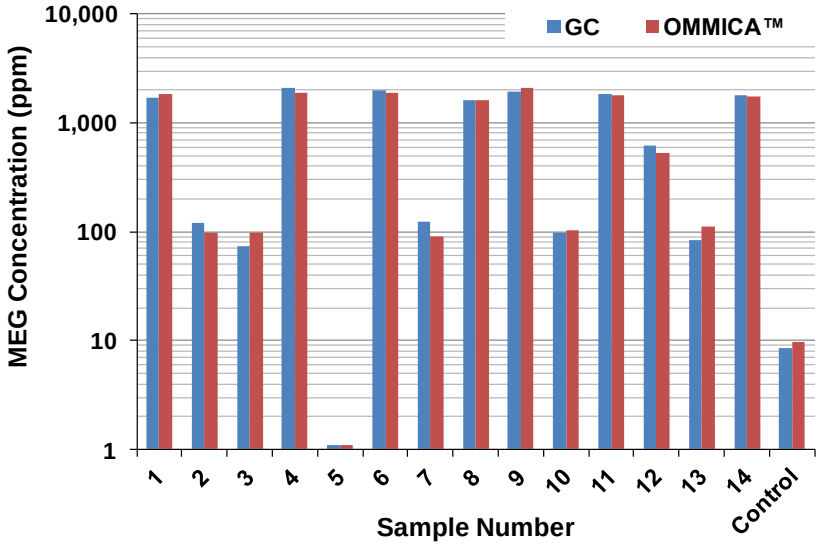

Figure 14. Results from analysis of MEG in water samples from a regeneration facility by GC and OMMICA™.

Conclusions

The use of OMMICA™ kits to determine the concentration of methanol and MEG in produced fluids has been demonstrated and shown to work well for both aqueous and oil / condensate samples. OMMICA™ offers many advantages over traditional GC techniques, including its simplicity and use of robust equipment; it is therefore particularly suitable for offshore. The use of an automated extraction step in the OMMICA™ approach also gives increased confidence in the consistency of data obtained, particularly where different users may be analysing samples. Finally, it is recognised that the complexity of oil field fluids means monitoring systems need to be robust to potential interferences, we have shown here that even chemically similar compounds do not interfere with the OMMICA™ method.

The results from an offshore methanol in produced water trial, where the samples were analysed by OMMICA™ (offshore) and GC (after shipping onshore), showed an excellent match between the two techniques. The methanol concentrations determined by OMMICA™ were slightly higher but this is believed to be because of the time difference (>6 weeks) between the two sets of analyses. This decrease in methanol concentration with time was also seen for oil samples, highlighting the importance of measuring samples as soon as possible after collection to generate an accurate representation of methanol content. The results from a MEG in water field trial, where samples were taken on a MEG regeneration facility, also showed excellent comparison between GC and OMMICA™.

Acknowledgements

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