Quantitative Discharge Water Analysis using Mobile ¹H NMR



Motivation

Discharge water is an inevitable byproduct stream associated with oil and gas extraction. The economic and efficient disposal of this water is critical and has to comply with environmental legislation regarding hydrocarbon content. Subsea separation has the potential to unlock significant hydrocarbon resources offshore¹, but this potential is limited

by the available methods for measuring the quality of the separated phases, in particular the water phase. A **new approach** is needed which is

Reliable Robust Compact **On-line** Sensitive to ppm levels Self-calibrated











Figure 1. (a) Shows the increase in global onshore and offshore produced water² and (b) a schematic of a subsea operation platform.³ Increased subsea separation diminishes cost associated with pumping large volumes of water to the surface.

Experimental Background

Validation of Methodology

1. SPE for pre-concentration and separation of contamination from water matrix



Figure 2. Schematic of the applied reversedphase SPE procedure with four steps (1) Loading (2) Removal of residual H_2O with compressed air and (3) Eluting

2. Quantitative analysis with benchtop ¹H NMR: Pulse and collect sequence & analysis of frequency domain spectrum



Figure 3. Spectrum of crude oil in the selected solvent system consisting of 1 % v/v CHCl₃ in PCE (C_2Cl_4) after SPE. Chemical shift resolution is sufficient to clearly distinguish the two resonances of approximately equal magnitude.

100

80

NMR

GC-FID



Figure 4. Shows a schematic of a half-automated extraction system combined with NMR and IR analysis.



40 ¬ NMR GC-FID 35 ▲ IR 30 ב 25 ממ _<u>≓</u> 20 లి 15 10 sample

Figure 7. Average concentration of crude oil in contaminated water (independent batches 1, 2 and 3) determined via SPE-NMR, SPE-IR and GC-FID analysis. Error bars result from measurements in triplicate for each of the applied methods.



Aromatic & Aliphatic Quantification

Approach: Two references with distinct chemical shift in two solvent systems at specific ratios.⁶

2.3

 \rightarrow Twofold SPE allowing simultaneous quantification of aromatics and aliphatics via change in







Figure 8. Spectra of hexane and toluene in (a) solvent mix 1 - 1 % CHCl₃ and 0.175 % HMDSO $(C_6H_{18}OSi_2)$ v/v in PCE and **(b)** solvent mix 2 – 1.5 % CHCl₃ and 0.1 % HMDSO v/v in PCE. Chemical shift resolution allows us to robustly distinguish the aromatic group ($\delta \approx 6-9$) and the aliphatic peaks ($\delta \approx 0 - 3$).



1250

<mark>ੇ</mark> 1000

750

500





Figure 10. Average concentration of total oil, aromatic hydrocarbons and aliphatic hydrocarbons in two independent batches A and B (crude oil & toluene in water) as determined via ¹H NMR and GC-FID. Error bars represent the standard deviation across three repetitions.

Prototype Development & Field Trial (Pluto LNG)



Figure 11. Operation of the Spinsolve outside the lab in the plant. (a) Spinsolve set up next to sampling device in close proximity to plant equipment (24 – 28 °C, 15 – 60 % rel. humidity). (b) Magnet operating with stable shim and good SNR.

Conclusions

- Proof-of-concept SPE-NMR for determination of oil in water at ppm level
- ✓ Simultaneous aromatic & aliphatic quantification
- ✓ Semi-automated prototype & NMR successfully trialled at onshore gas plant

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for the daily samples. On the second vertical axis, the level in the historical and current data and daily averages measured with oily water tank (samples were taken from this tank) is plotted SPE-NMR, LLE-NMR and LLE-IR. over the period of the field trial. Error bars represent the standard deviation across repeated measurements where applicable.

Future Work

- Flow-through qNMR measurements Bench scale tests to maximize
- Development of climate control box

for enhanced magnet robustness

instrument lifetime

Onshore field trials with an autonomous device

References

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