# Quantitative Discharge Water Analysis using Mobile $^{1}$H NMR

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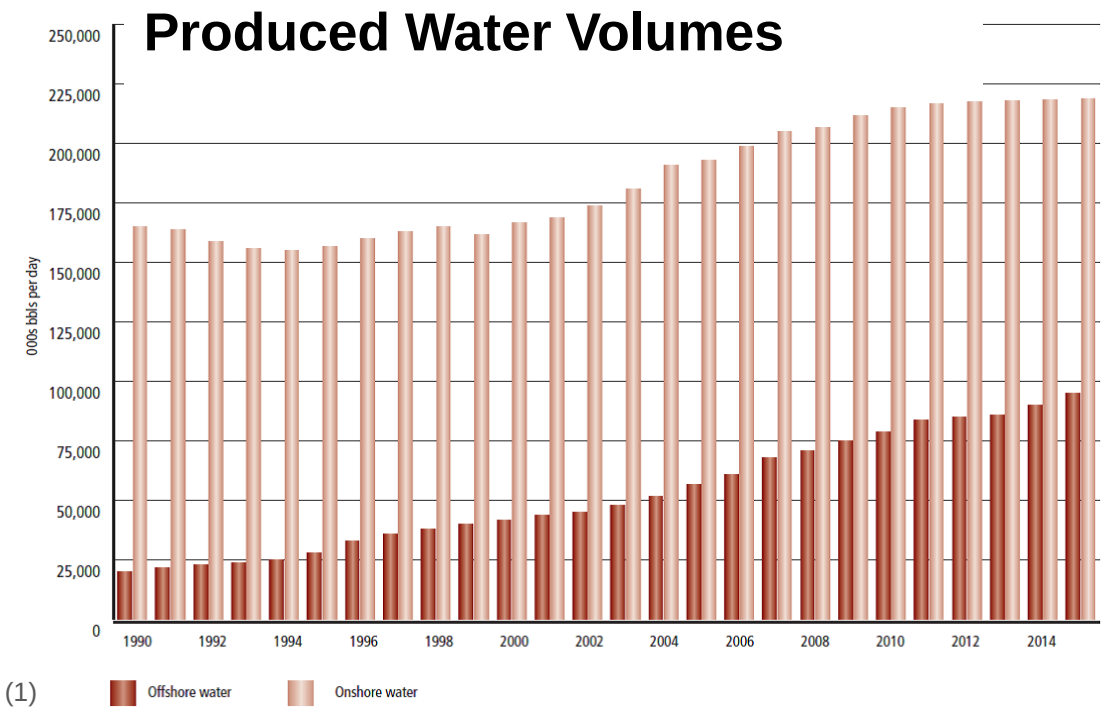
**SUT Evening Technical Meeting, Perth**

**11th April 2018**

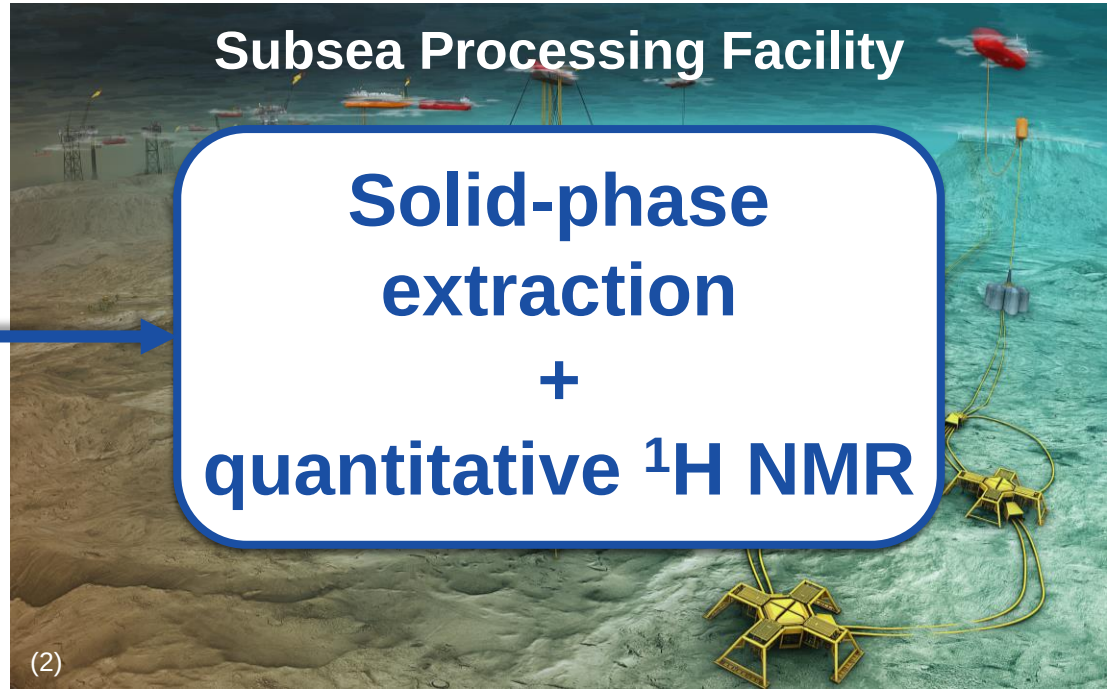
# Subsea Oil-in-Water Measurements




(1)

**(Subsea) processing & separation**

**Produced water (PW) offshore / subsea → Discharge**




(2)

**Aliphatics**

**Aromatics**

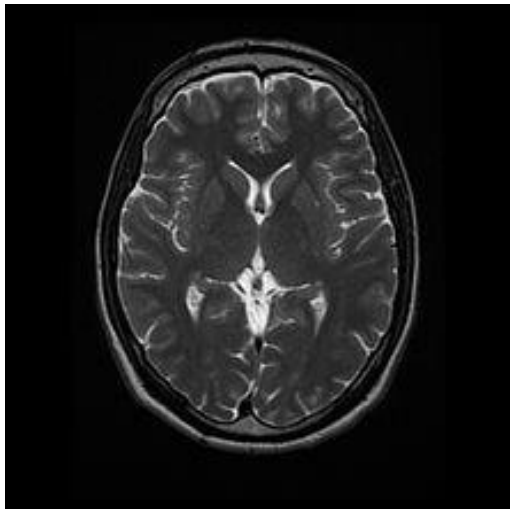
*(1) Dal Ferro, B. and Smith, M. 2007. Global onshore and offshore water production. Oil & Gas Review OTC Edition (2) https://www.technipfmc.com/en/media/media-gallery*

# $^{1}$H Nuclear Magnetic Resonance (NMR)

## Basic theory


Imaging

**MRI = NMR Imaging**




NMR

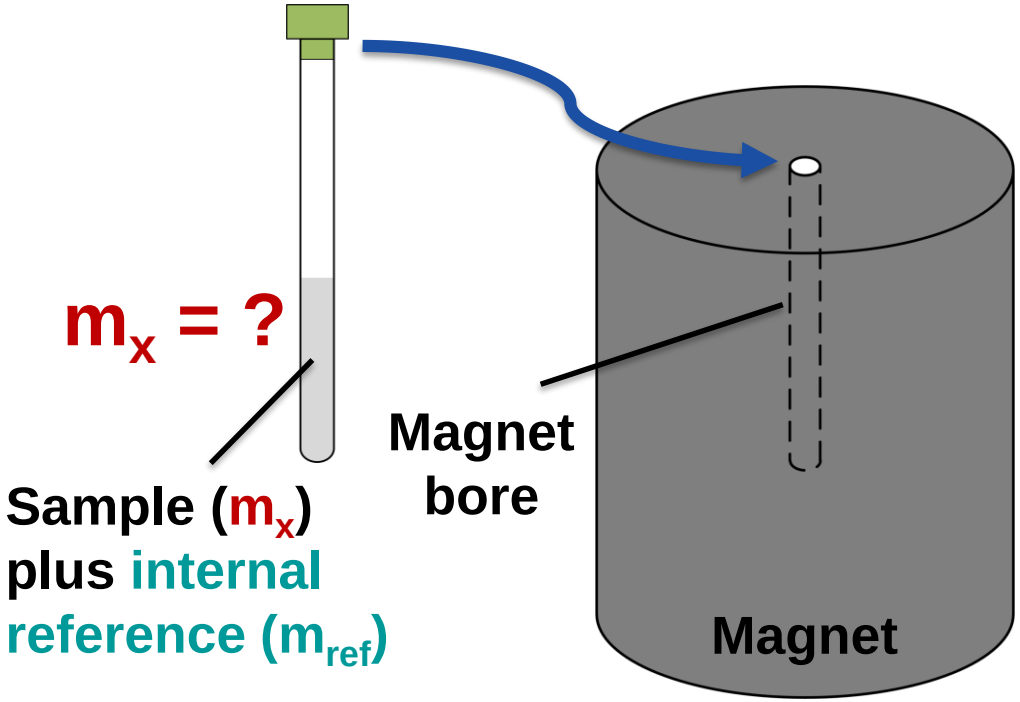
**$^{1}$H NMR**

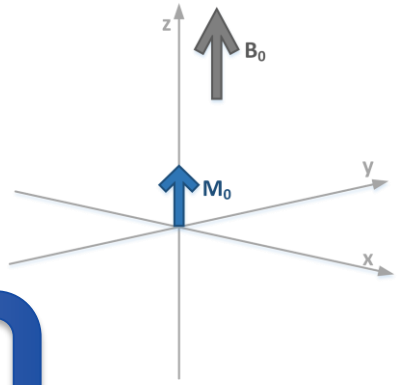
**Measurement of the magnetic moment of hydrogen nuclei ($^{1}$H)**

**Petroleum Hydrocarbons**

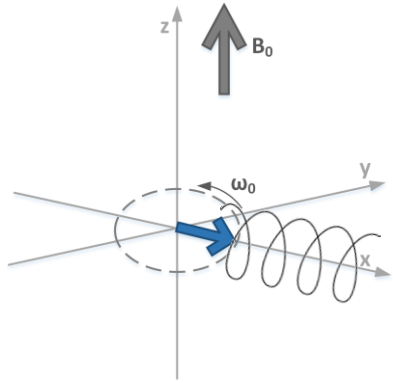
# $^1$H NMR Spectroscopy

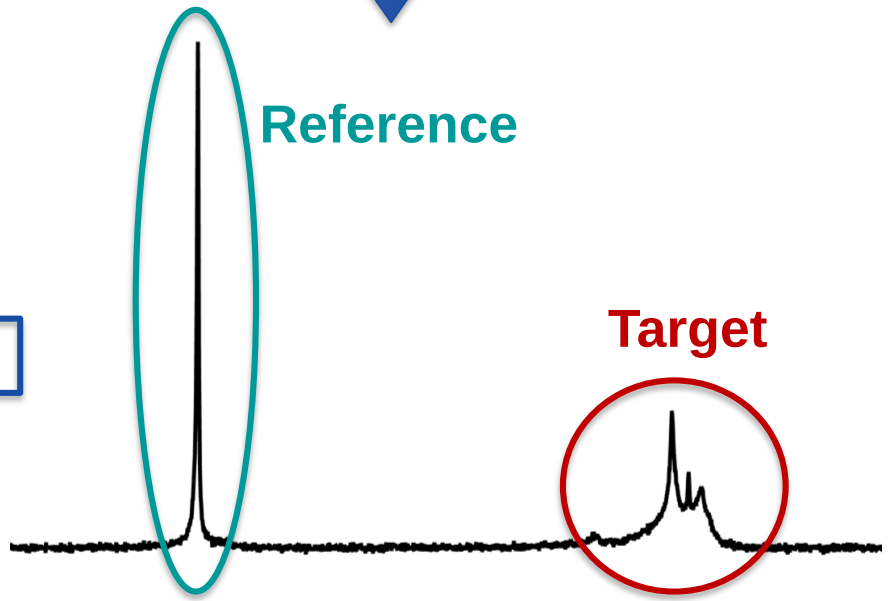
## Quantitative Analysis




**Excitation & detection**




**Signal ~ Number $^1$H**

**$m_x$ = … mg**

# Low field benchtop $^{1}$H NMR

## Characteristics for PW analysis

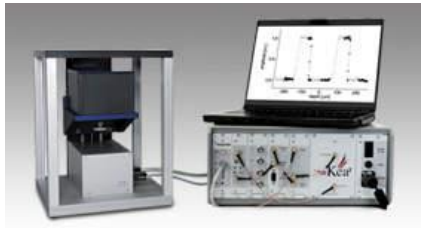
Earth field

50 µT

Minispec

0.5 T

Mouse



0.3 – 0.7 T

- **Low-field = reasonably priced (<$100k), compact, mobile**
- **Non-destructive**
- **<u>Non-optical</u>**
- **Dissolved and dispersed oils**
- **<u>Self-calibrating</u> if internal reference present**

**Spinsolve**


$$B_0 = 1\,T$$

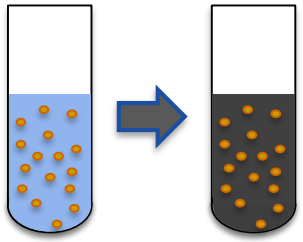
$$\emptyset_{bore} = 5\,mm$$

$$T_{magnet} = 28.5℃$$

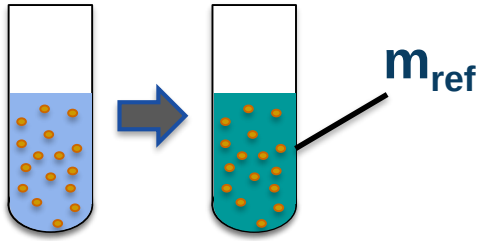
# Solid-phase extraction (SPE)

## Motivation and procedure

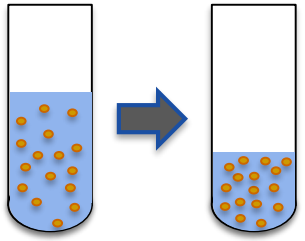
**Extraction from aqueous phase**



**Transfer into suitable solvent**




**Pre-concentration**

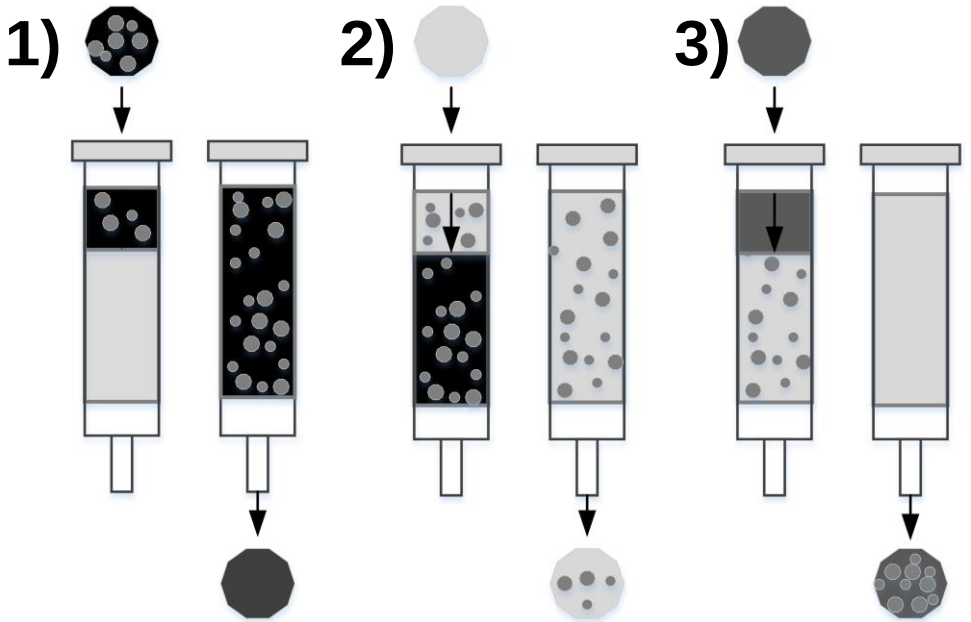


**Reversed-phase SPE**

→ Low selectivity

→ Non-polar, hydrophobic interactions

→ Aqueous samples




# 3) Elution

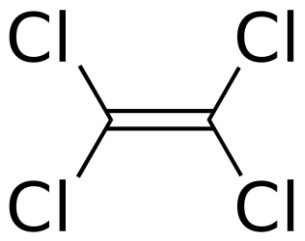
# Solid-phase extraction (SPE)

## Solvent for elution & NMR measurement

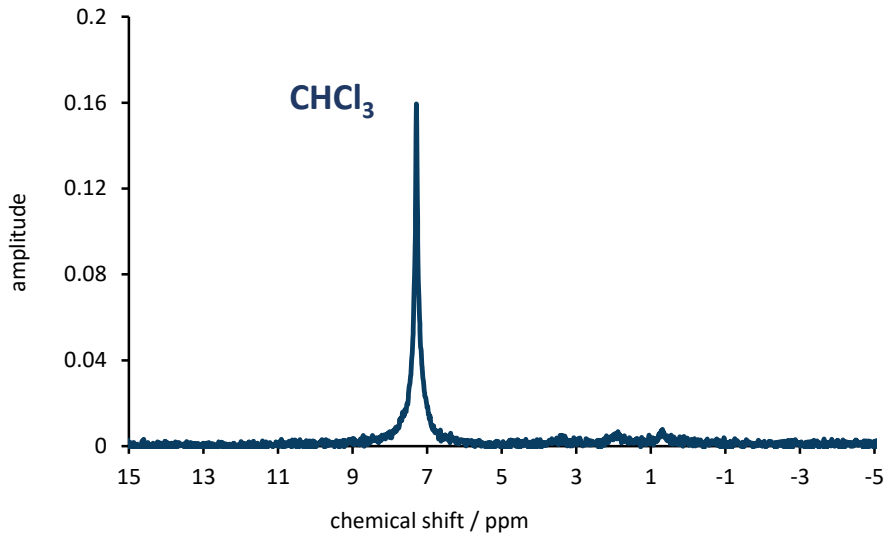
### 3) Elution:

### Tetrachloroethylene (PCE) with 1% v/v $CHCl_3$

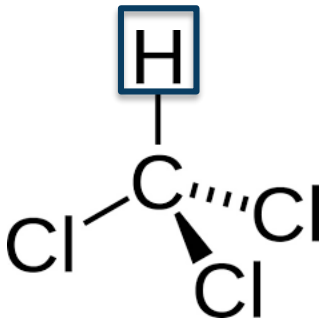
**Base solvent**




**NO peak**



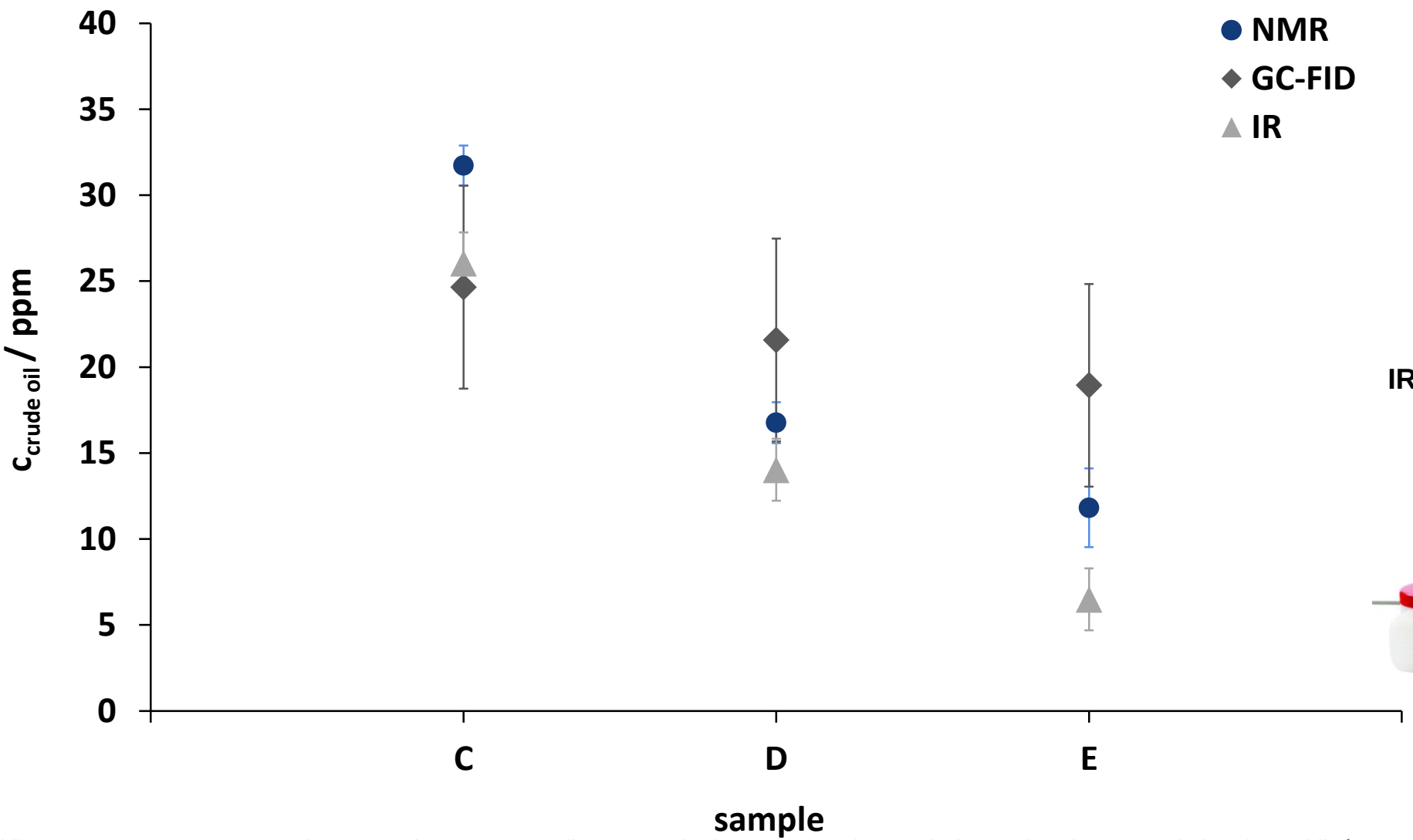

**Reference**




**1 sharp peak**

# Proof-of-concept

## $H_2O$ contaminated with crude oil

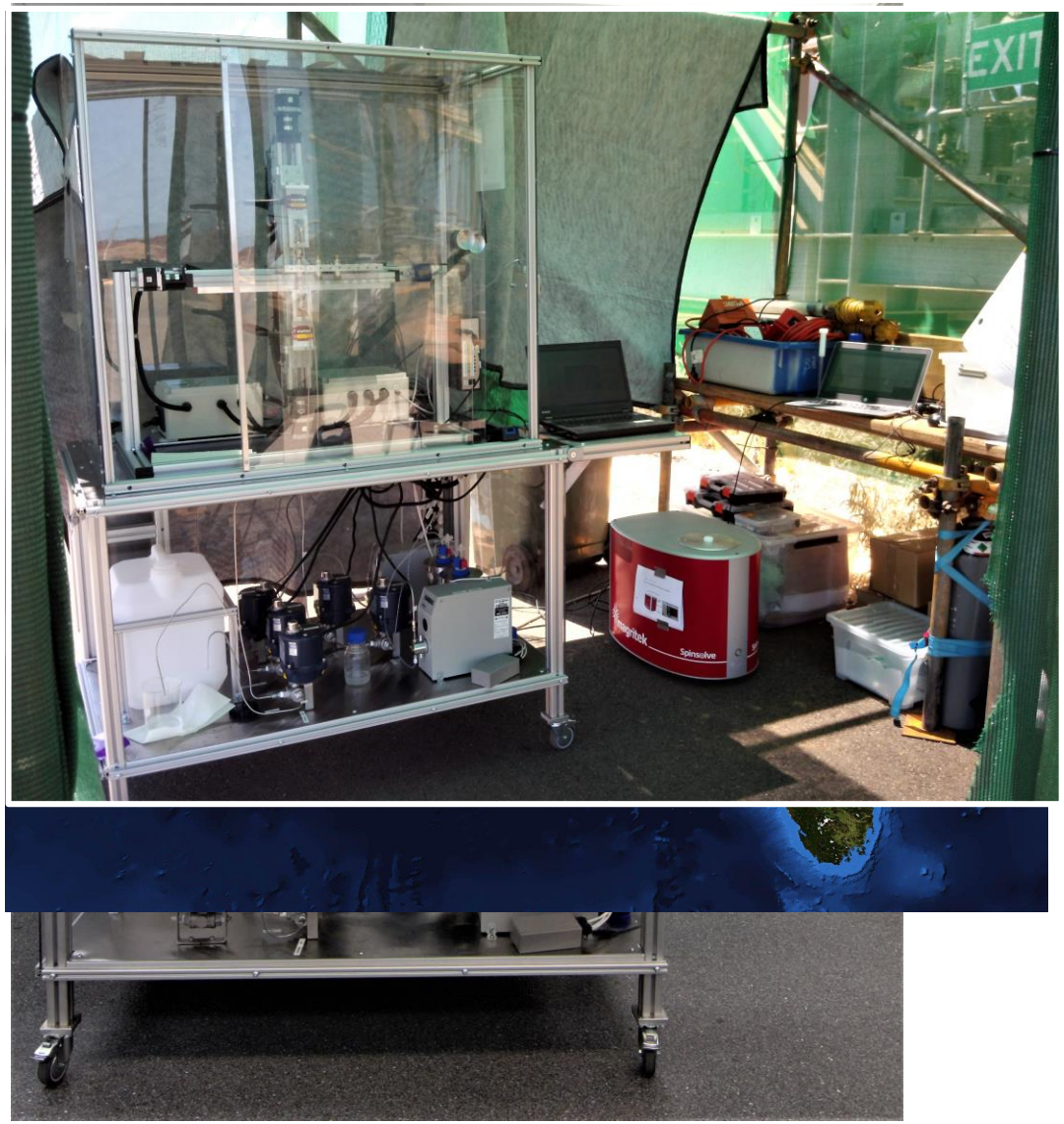




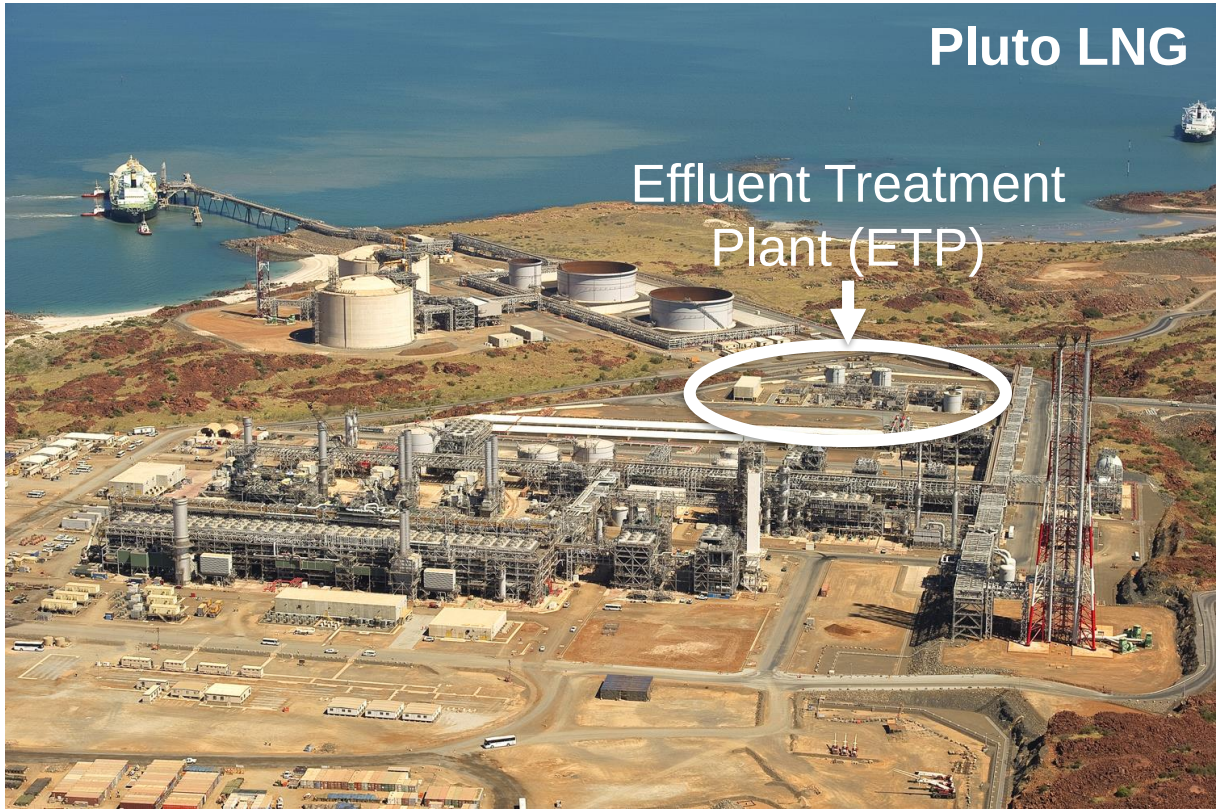

Wagner, L., Kalli, C., Fridjonsson, E.O., May, E.F., Stanwix, P.L., Graham, B.F., Carroll, M.R.J. and Johns, M.L. (2016), Quantitative Produced Water Analysis using Mobile $^{1}$H NMR, *Meas. Sci. & Tech.*, 27, 105501.

# Field trial – Onshore gas plant

## *Self-contained transportable* from Perth to Karratha



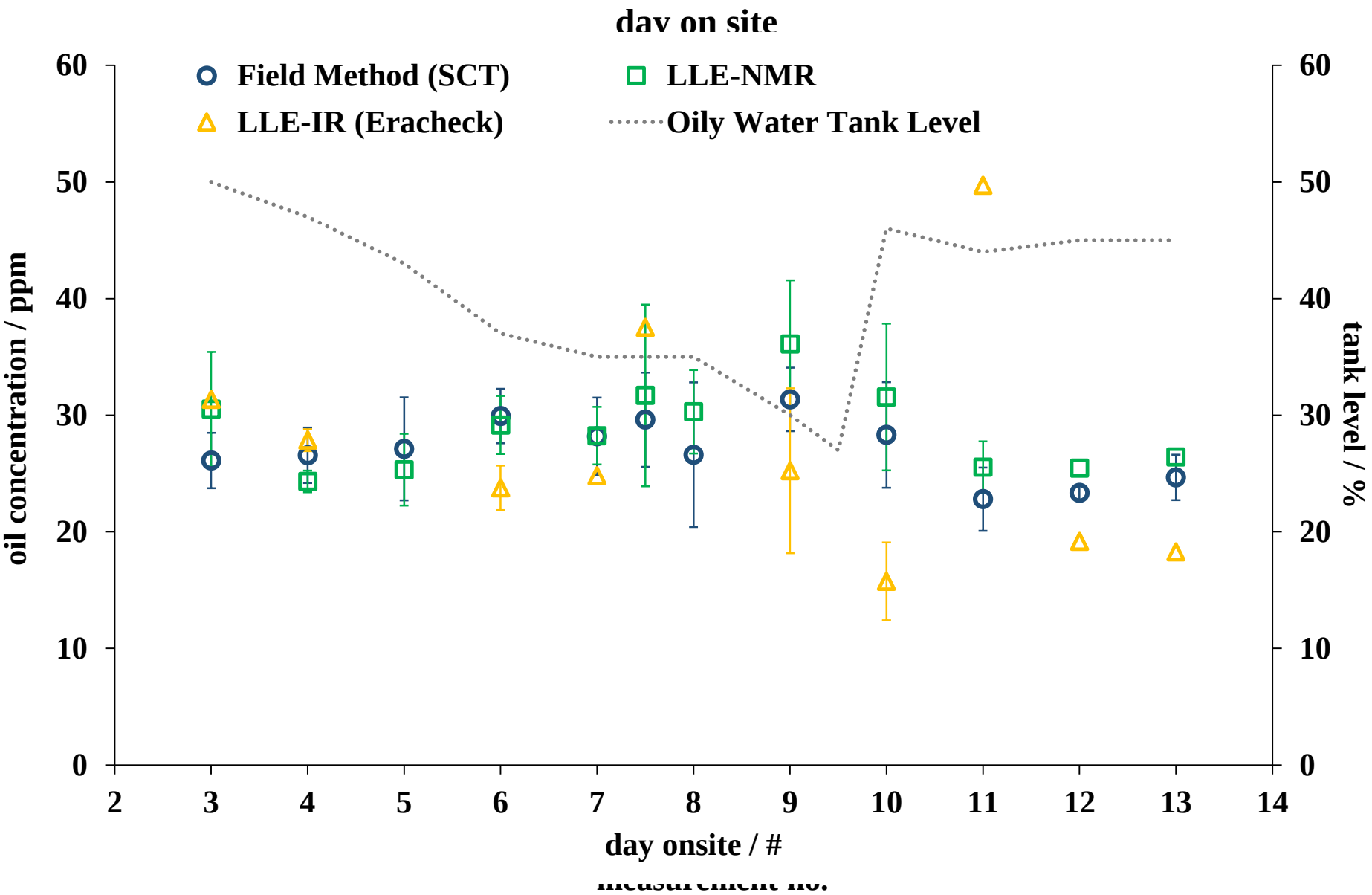

**Sampling location: Oily Water Tank**

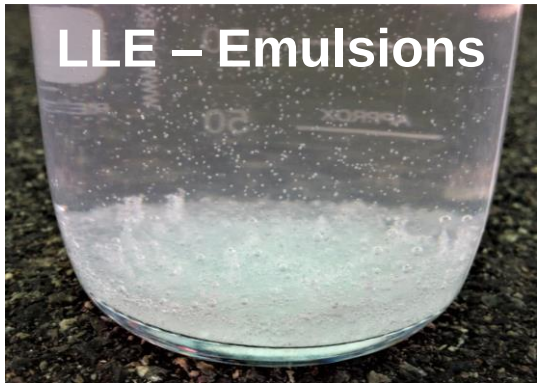



- LLE + IR (Eracheck)

# Field trial – Onshore gas plant

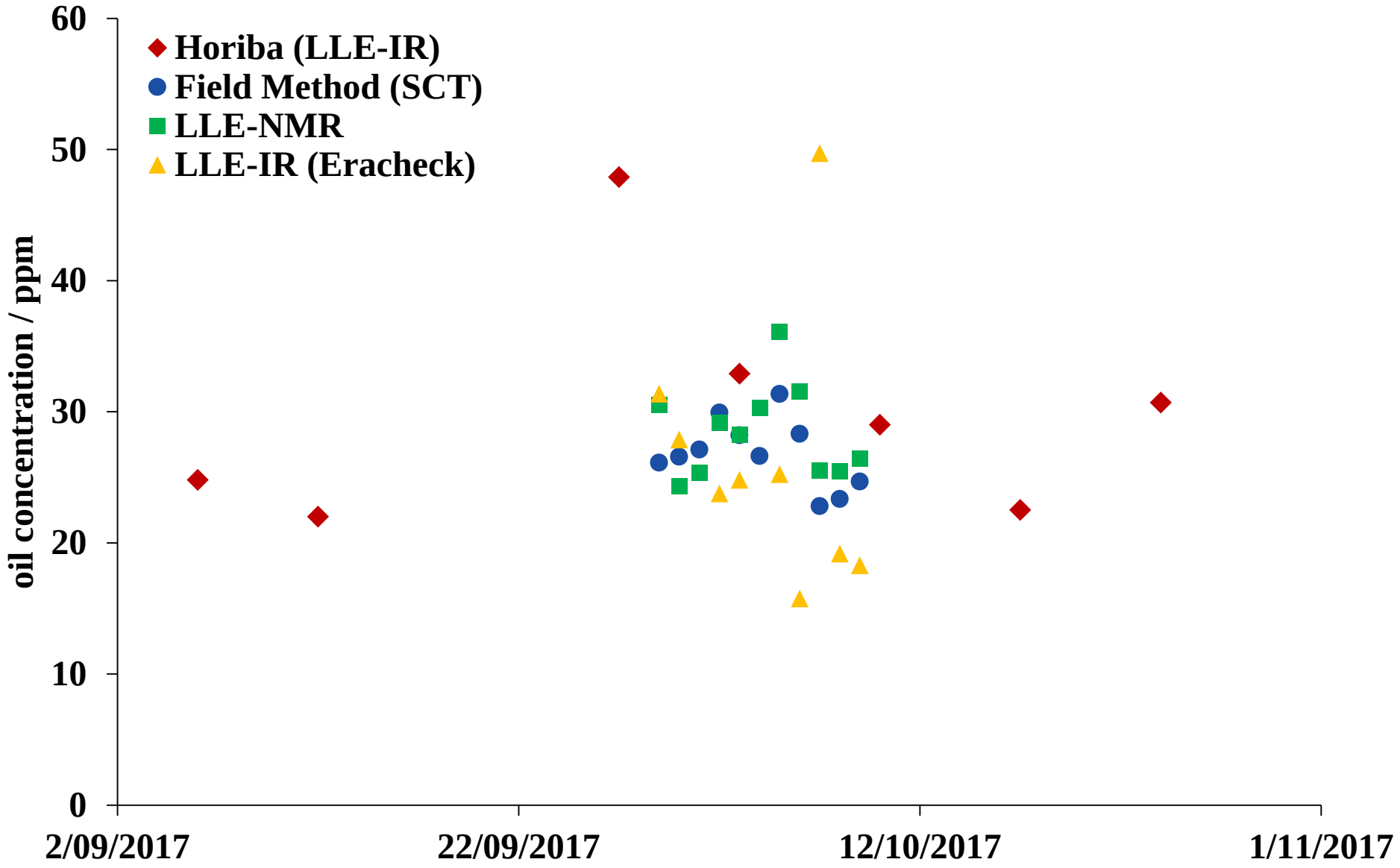
## Results – Daily averages




# Field trial – Onshore gas plant

## Comparison with independent laboratory



# Field trial – Onshore gas plant

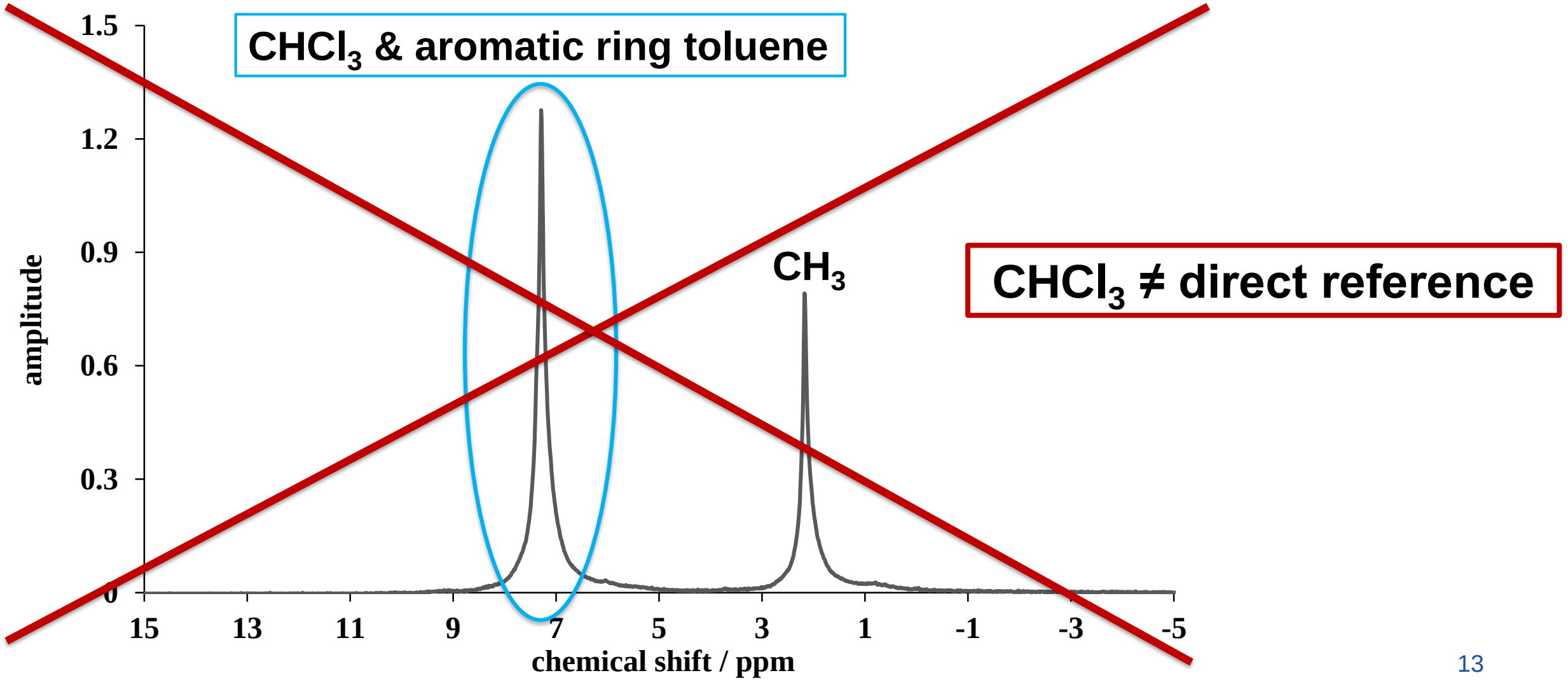
## Summary

- ✓ No faults
- ✓ 36 hours continuous operation
- ✓ NMR operates outside laboratory
- ✓ Good agreement with
  - ✓ Independent measurements
  - ✓ Industry standard – Horiba measurement

# Aromatic / aliphatic quantification

## Approach for separate quantification

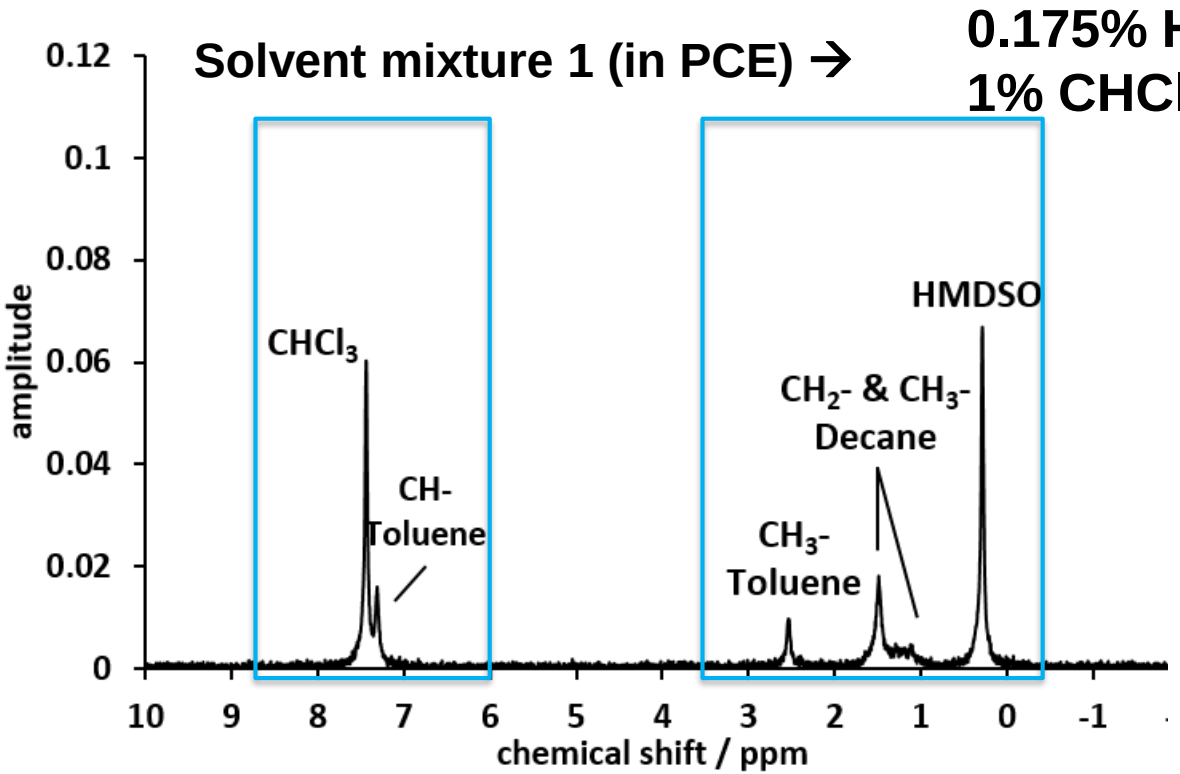
**Toluene in PCE + $CHCl_3$ solvent**




**$CHCl_3$ ≠ direct reference**

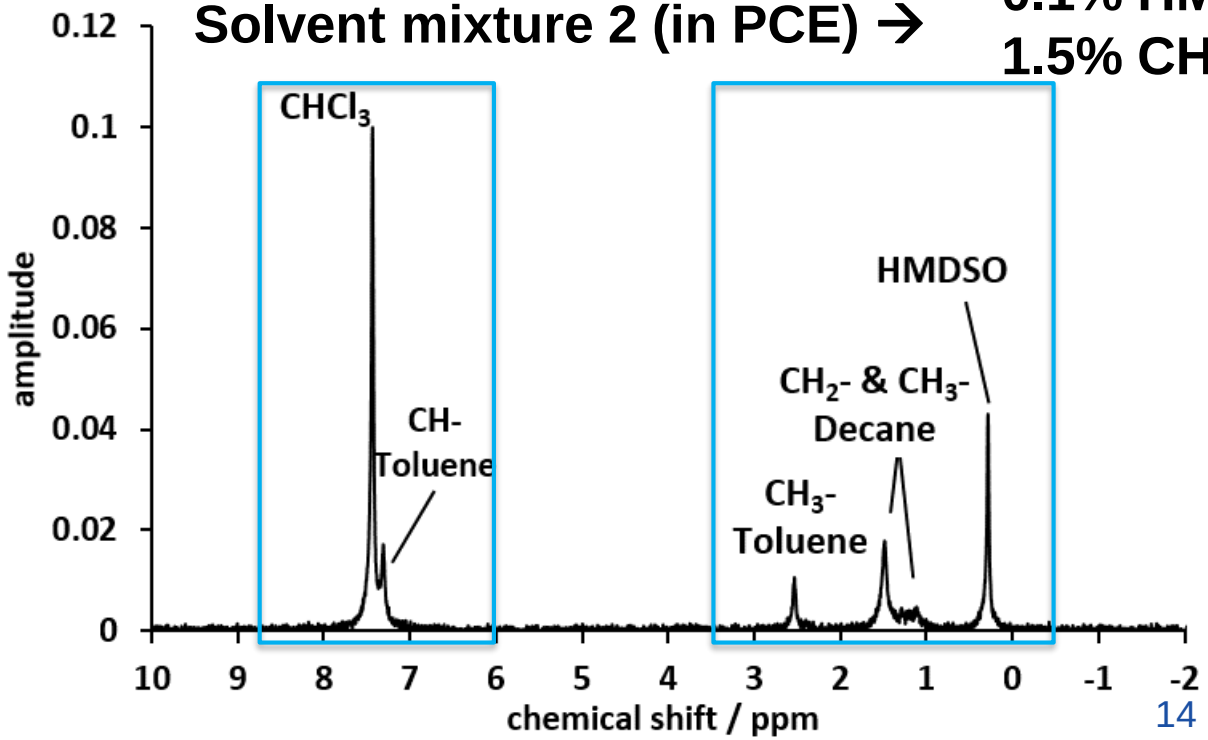
# Aromatic / aliphatic quantification

## Approach for separate quantification




**Reference ratios**

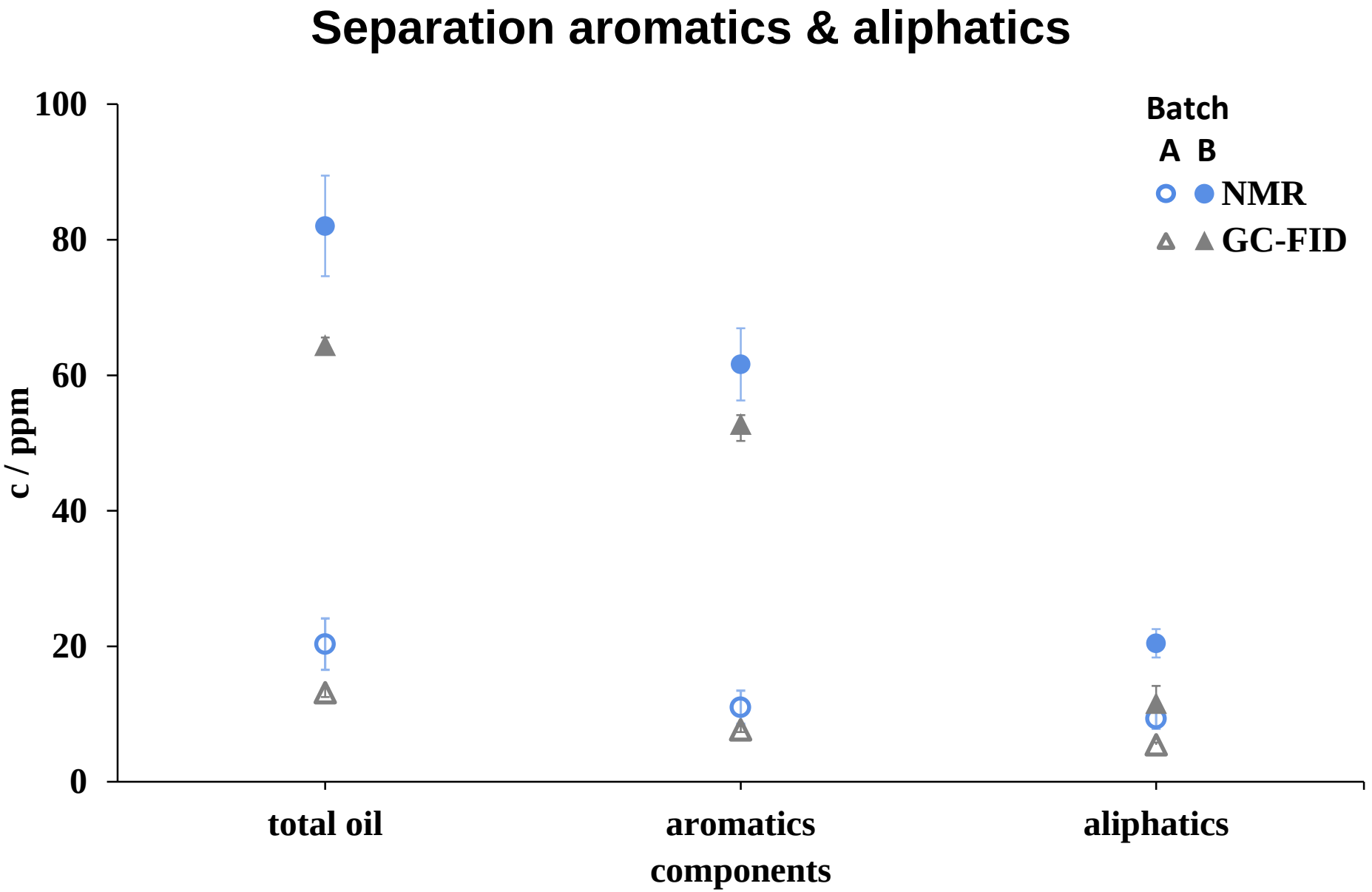
$$r_1 \& r_2 = const.$$




**Contamination added:**
**+ 860 ppm toluene**
**+ 730 ppm decane**

# $H_2O$ contaminated with toluene & oil

## NMR vs GC-FID



# Conclusions & future work

- ✓ **Proof-of-concept SPE-NMR for OiW measurements**
- ✓ **Low maintenance measurement procedure**
  - ✓ **Self-calibrated**
  - ✓ **Non-optical**
  - ✓ **SPE cartridges recyclable**
  - ✓ **Solvent reusable**
  - ✓ **Readily automated**
- ✓ **Quantification of aromatics and aliphatics**
- ✓ **Semi-automated prototype successfully trialled on an onshore gas plant**

- ➢ **Development into fully automated prototype**
- ➢ **Maximizing life-time of prototype**

# Acknowledgements

**Funding**

Chevron

UWA (*SIRF & AD-HOC scholarship)*

**Field Trial**

Woodside for provision of their plant & assistance throughout the process

**Guidance / Assistance**

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*Prof Eric May*

*Dr John Zhen*

*Chris Kalli*

FLUID SCIENCE & RESOURCES

THE UNIVERSITY OF WESTERN AUSTRALIA

# Thank you for the attention!

# QUESTIONS?