The Effects of Methanol on the Measurement of Oil and Grease in Produced Water With Portable Meters

by

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Objective

The objective of this study was to determine if the presence of low concentrations of methanol in produced water had a significant effect on the routine field monitoring of oil and grease concentration in produced water with portable meters.

Plan

Phase 1: Formulated Samples

Formulated samples with known concentrations of oil and methanol were created. The matrix consisted of oil concentrations of 0, 15, 30 and 60 mg/L, and methanol concentrations of 0, 20, 100 and 500 ppm. The 16 different formulated samples were analyzed for oil and grease concentration using the lab method and portable meters.

Phase 2: Field Samples

Field samples were collected from three different platforms and analyzed for oil and grease concentration using the lab method and portable meters. The samples were collected from platforms that had 1) no methanol in produced water, 2) typical methanol in produced water, and 3) elevated methanol in produced water; regarded as platforms "X", "Y" and "Z". Platforms "Y" and "Z" use methanol for hydrate inhibition in deepwater subsea wells and flowlines. Platform "Z" was sampled at a time of relatively high methanol use.

Methods / Equipment:

Analyses of oil and grease concentration with portable meters were performed using the Wilks Horizontal Attenuated Total Reflection (HATR) meter with a cubic zirconia trough plate and the Wilks Cuvette Holder Analyzer (CVH) meter with a 10 mm quartz cuvette cell.

The Wilks HATR meter is a plate model meter, where the extraction solvent is deposited on a plate and then allowed to evaporate. The remaining residue deposited on the plate is then analyzed to determine an absorption value that is correlated to oil and grease concentration. Vertrel MCA was used as the extraction solvent.

The Wilks CVH meter is a cuvette model meter, where the extraction solvent is placed in a cuvette. The cuvette is placed in the meter and then analyzed to determine an absorption value that is correlated to oil and grease concentration. Freon-113 was used as the extraction solvent.

The field meters were calibrated with "3-in-1" oil. Procedures that were used for the field sample extractions are found at www.oilfieldanalytics.com. The field sample extractions and meter analyses were performed at an onshore laboratory.

Laboratory analyses of oil and grease concentration were performed by EPA Method 1664A-HEM (n-Hexane Extractable Material, gravimetric analysis).

Results

Phase 1: Formulated Samples

The matrix of formulated samples and the corresponding lab and meter analytical results are presented in table 1.

spiked		Lab 1664A	plate model	cuvette model
oil	methanol	(O&G)	(O&G)	(O&G)
(mg/L)	(ppm)	(mg/L)	(mg/L)	(mg/L)
0	0	0	0	0
0	20	0	0	0
0	100	0	0	0
0	500	0	0	0
15	0	14	18	12
15	20	12	22	14
15	100	14	17	10
15	500	12	16	10
30	0	30	30	33
30	20	24	32	34
30	100	29	27	38
30	500	27	35	35
60	0	59	58	58
60	20	62	60	58
60	100	58	53	54
60	500	63	54	60

Table 1: Summary of Formulated Sample Analytical Results

A chart of the formulated sample analytical results is presented in figure 1.

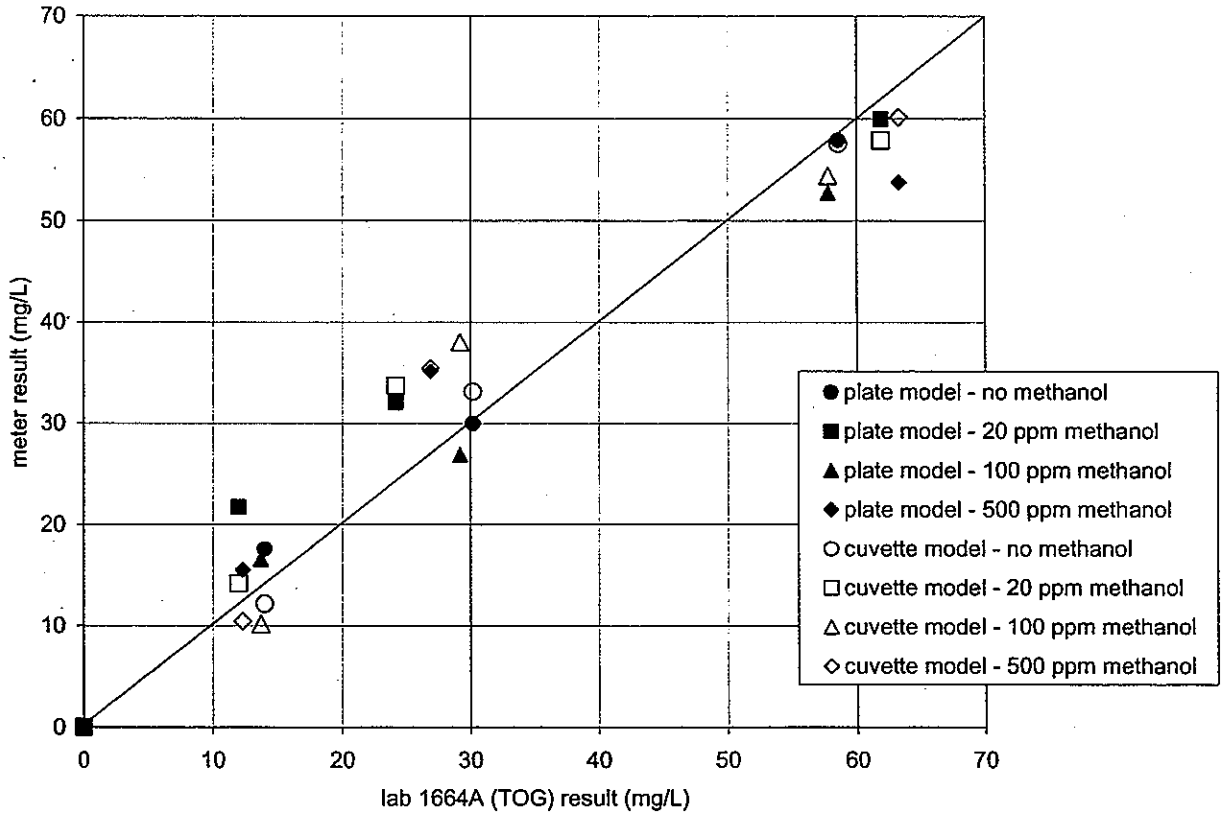

Figure 1: Analysis of Formulated Sample Analytical Results

Phase 2: Field Samples

The concentrations of methanol in the produced water effluent at the three platforms are presented in Table 2.

Platform	*Average Methanol Concentration (ppm)*	*Comments*
X	<100	Below Detection Limits
Y	565	
Z	655	First sampling event
Z	3750	Second sampling event

Table 2: Summary of Methanol Concentrations Observed in Produced Water Effluent

Field samples were collected and shipped to an onshore lab where they were analyzed by EPA Method 1664A-HEM and with portable meters. Results of the field sample lab and meter analyses are presented in table 3 and figure 2.

	extraction solvent	average methanol (ppm)	average O&G (mg/L)	ratio of meter to lab result	ratio of cuvette to plate model result
Platform X					
Methanol		*<100*			
Lab (Method 1664A)	hexane		88.0		
meter - plate model	vertrel		82	0.93	
meter - cuvette model	freon		87	0.99	1.06
Platform Y					
Methanol		565			
Lab (Method 1664A)	hexane		*(no result)*		
meter - plate model	vertrel		39	*(n/a)*	
meter - cuvette model	freon		40	*(n/a)*	1.03
Platform Z					
Methanol		3750			
Lab (Method 1664A)	hexane		20.1		
meter - plate model	vertrel		23	1.14	
meter - cuvette model	freon		42	2.09	1.83

Table 3: Summary and Analysis of Field Sample Analytical Results

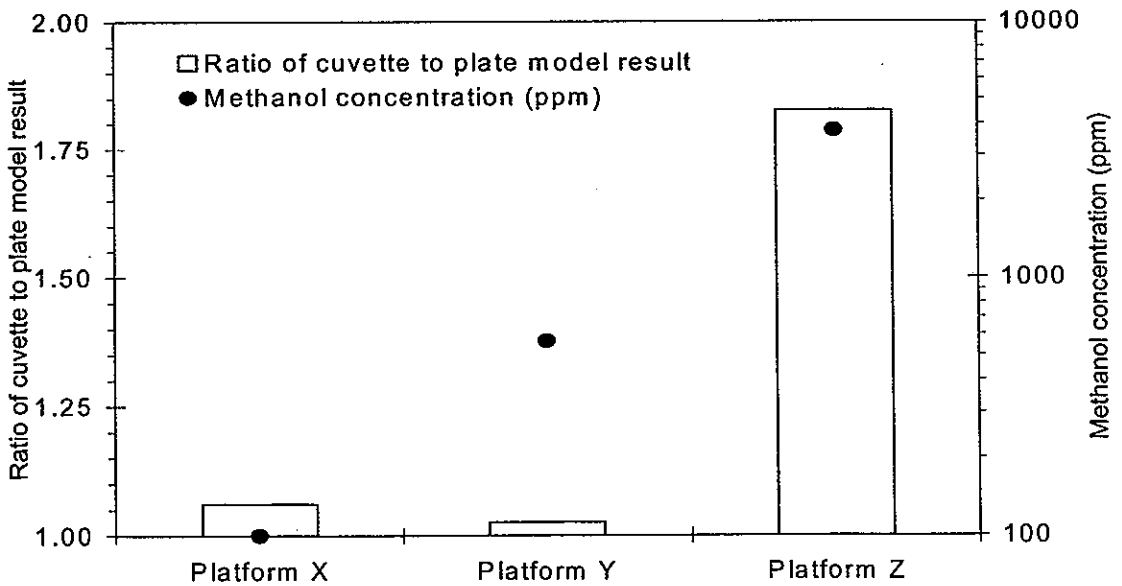

Figure 2: Analysis of Field Sample Analytical Results

Observations and Conclusions

The analyses of formulated samples indicated that the presence of methanol did not have a significant effect on measurements of oil and grease concentration using portable meters, at the concentrations of methanol tested, which ranged up to 500 ppm.

The concentration of methanol was higher than initially suspected in field samples of treated produced water effluent at production platforms which use methanol for hydrate inhibition of deepwater subsea wells.

The analyses of field samples indicated that the presence of relatively high concentrations of methanol (~3750 ppm) had an effect on measurements of oil and grease concentration using a cuvette model meter, but not when using a plate model meter. The observed effect was an overestimation, by a factor of 2, of the oil and grease concentration when analyzed with the cuvette model meter.

Analyses performed on methanol mixed directly with solvent (without a water-solvent extraction) with plate and cuvette model meters indicated that methanol is detected by the cuvette model meter with sensitivity similarly to the detection of oil.

The results of this study indicated that methanol in produced water samples was not efficiently extracted (remained predominantly in the water) and/or was evaporated during the water-solvent extraction procedure.

The relatively low concentration of methanol that was extracted during the water-solvent extraction appeared as an increased absorbance (therefore an increased oil and grease concentration) when analyzed with the cuvette model meter, but was presumed to have evaporated with the solvent when analyzed with the plate model meter.

Ideas for future studies include 1) collecting field samples from a platform without methanol, then spiking the samples with known concentrations of methanol and analyzing them at the platform with portable meters; and 2) evaluating whether the presence of methanol somehow reduces the measured concentration of oil and grease by lab gravimetric analysis.

Acknowledgements

The authors would like to recognize the following contributors to this study:

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January 16, 2003

WILKS ENTERPRISE, Inc.
Applying Infrared Technology to the Real World

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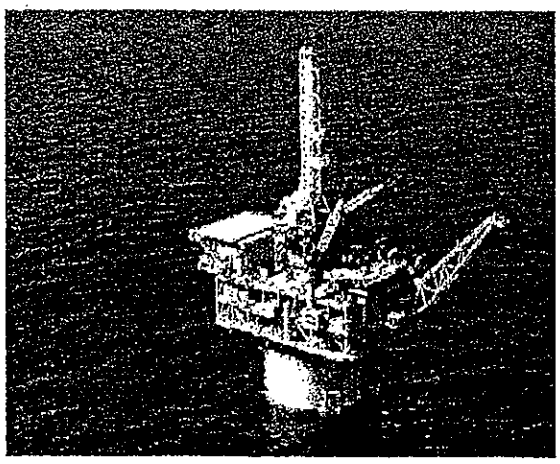

Plan

- Phase 1: Formulated Samples
  - Known concentrations of oil and methanol
  - Oil concentrations of 0, 15, 30 and 60 mg/L
  - Methanol concentrations of 0, 20, 100 and 500 ppm
- Phase 2: Field Samples
  - Collected from three different platforms
    1) platform "X" - no methanol in produced water
    2) platform "Y" - typical methanol in produced water
    3) platform "Z" - elevated methanol in produced water
  - Platforms "Y" and "Z" use methanol for hydrate inhibition in deepwater subsea wells and flowlines
  - Platform "Z" sampled at a time of relatively high methanol use

Methods / Equipment

- Wilks Horizontal Attenuated Total Reflection (HATR) meter with a cubic zirconia trough plate
  - plate model meter
  - extraction solvent is placed on a plate and then allowed to evaporate
  - remaining residue deposited on the plate is then analyzed to determine an absorption value that is correlated to oil and grease concentration
  - Vertrel MCA was used as the extraction solvent.
- Wilks Cuvette Holder Analyzer (CVH) meter with a 10 mm quartz cuvette cell.
  - cuvette model meter
  - extraction solvent is placed in a cuvette
  - cuvette is placed in the meter and then analyzed to determine an absorption value that is correlated to oil and grease concentration
  - Freon-113 was used as the extraction solvent.
- Laboratory analyses performed by EPA Method 1664A-HEM (n-Hexane Extractable Materials, gravimetric analysis).

Results – Phase 1: Formulated Samples

spiked oil (mg/L)	spiked methanol (ppm)	Lab 1664A (O&G) (mg/L)	plate model (O&G) (mg/L)	cuvette model (O&G) (mg/L)
0	0	0	0	0
0	20	0	0	0
0	100	0	0	0
0	500	0	0	0
15	0	14	18	12
15	20	12	22	14
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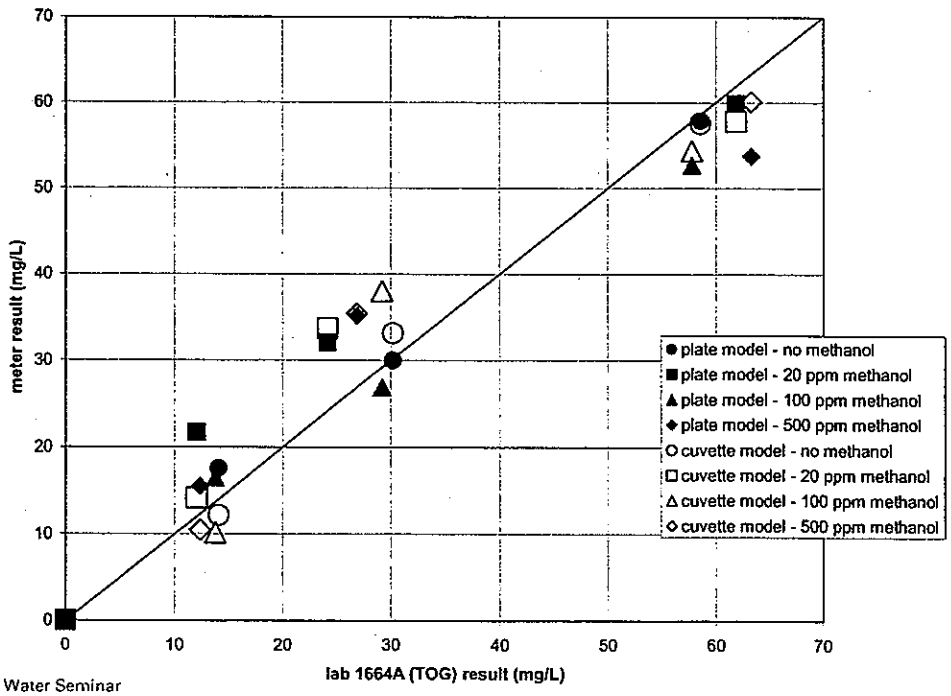
Analysis of Formulated Sample Analytical Results



Results – Phase 2: Field Samples

Platform	*Average Methanol Concentration (ppm)*	*Comments*
X	<100 (BDL)	Below Detection Limits
Y	565	
Z	655	First sampling event
Z	3750	Second sampling event

Summary and Analysis of Field Sample Analytical Results

	extraction solvent	average methanol (ppm)	average O&G (mg/L)	ratio of meter to lab result	ratio of cuvette to plate model result
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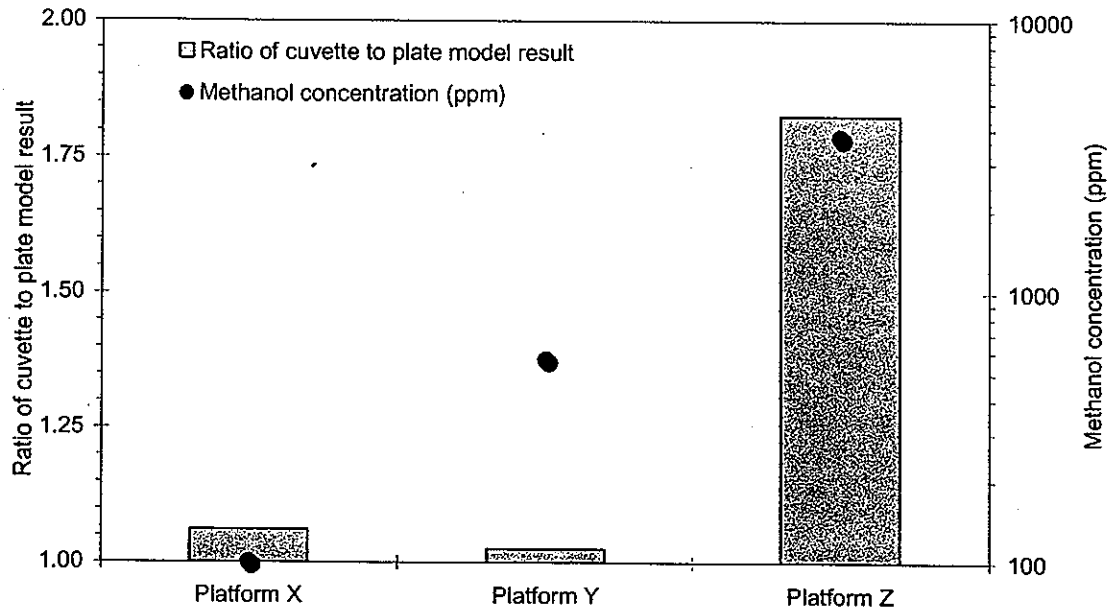

Observations

- Formulated samples - methanol had no observed effect on measurements of oil and grease concentration (at the concentrations of methanol tested, up to 500 ppm).
- Field samples - relatively high concentrations of methanol (~3750 ppm) had an observed effect on measurements of oil and grease concentration when using a cuvette model meter, but not when using a plate model meter. The observed effect was an overestimation of oil and grease concentration by a factor of 2.
- Methanol concentrations in field samples of treated effluent were higher than initially suspected.

Conclusions

- Methanol in produced water samples was not efficiently extracted (remained predominantly in the water) and/or was evaporated during the water-solvent extraction procedure.
- Ideas for future studies include:
  - Collecting field samples from a platform without methanol, and spiking the samples with known concentrations of methanol.
  - Evaluating whether the presence of methanol reduces the measured concentration of oil and grease by lab gravimetric analysis

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