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Project Summary

Field Test Kit for Oil-Brine Effluents from Offshore Drilling Platforms

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This research program was initiated to evaluate test methods for characterizing oil-brine effluents from offshore oil production platforms and to deliver to the U.S. Environmental Protection Agency (EPA) a field test kit for onsite oil-brine analyses. After an initial laboratory evaluation and selection of test methods and equipment, two onsite oil-brine analyses were conducted in Kenai, Alaska—one at the AMACO Dillon Offshore Production Platform, and the other at the Shell MGS Joint Onshore Facility.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Offshore drilling facilities are becoming increasingly numerous as new oil reserves are needed to replace depleted land-based sources. As a result, the potential for drilling and production accidents such as the Santa Barbara Channel disaster are also expected to increase. Another pollution concern is the presence of brine in the crude oil obtained from deep-well drilling sites. On offshore platforms, the crude oil is routinely passed through an oil/water/gas separator, and the brine is then discharged into the ocean. After varying degrees of additional treatment, this brine contains a fine suspension of oil droplets that is not removed in the separator. Inefficient brine treatment could result in a serious contamination source.

As one phase of a U.S. Environmental Protection Agency (EPA) contract with Exxon Research and Engineering, a study was made of pollution control technology for offshore drilling and production platforms, and test methods were recommended for characterizing oil-brine effluents.[1]

The Offshore Operator's Committee (OOC) reviewed the Exxon procedures and recommended several modifications.[2] Additional changes have been proposed and verified through field evaluation by Texas Instruments Incorporated.[3] A summary of the OOC test methods is given in Table 1.

This project was initiated as a means for evaluating the OOC methods and for developing a field kit for onsite oil brine analysis. Specifically, this work, conducted by Stanford Research Institute (SRI), has consisted of the following tasks:

1. Evaluate the OOC-modified test methods (Table 1, Status 1) for characterizing oil-brine effluents from offshore oil production facilities.
2. Recommend and package into a field test kit suitable equipment and instrumentation for conducting the oil-brine characterizations.

Table 1. OOC Test Methods for Characterizing Oil-Brine Effluents

Test No.	*Test*	*Method/Apparatus*	*Method Status**	*Type of Test*
1	Oil-in-water	Gravimetric; infrared	1	Field
2	Suspended solids	Filtration	3	Lab
3	Particle size	Microscopy	1	Field
4	Surface tension	Tensiometer	3	Field
5	Viscosity	Ostwald; Brookfield	3	Field
6	Specific gravity	Centrifuge; hydrometer	2	Field
7	Salinity	Centrifuge; titration	3	Field
8	pH	pH meter	3	Field
9	Temperature	Thermometer	3	Field
10	Brine composition	Atomic absorption	2	Lab
11	Bacterial culture	API RP-38	2	Lab
12	Oil separation	API 734-53	2	?
13	Soluble materials	Column and SiO_2 adsorption; spectrophotometry	1	Field
14	Flow rate	Shell PSM	2	Field

**Status 1: OOC-modified: Evaluate at SRI.*
Status 2: OOC-modified: Standard procedures.
Status 3: OOC-approved: Standard procedures.

3. Evaluate the field test kit at a suitable onshore or offshore oil production facility.
4. Deliver the field test kit to EPA with detailed instructions for performing the tests.

Evaluation and Selection of OOC Methods for Test Kits

The OOC-recommended test procedures, a brief description of them as suggested by the Texas Instruments report,[3] and our recommendations and modifications are summarized in Table 2. Tests of these OOC methods were conducted on July 7, 1980, at the Dillon offshore production platform, Platform, Kenai, Alaska, and on July 8, 1980, at the Shell MGS Joint Onshore Facility, Kenai, Alaska. Water samples were withdrawn for analysis from the final production water stream before discharge into the ocean. Field results were generally replicated three times during the 8-hour testing period.

Recommended Tests

The following OOC tests (Table 2) are included in the field test kit:

(1) Oil in water (infrared and gravimetric)
(2) Soluble materials (equilibration and filtration)
(3) Specific gravity
(4) pH
(5) Temperature
(6) Suspended solids
(7) Bacterial culture (includes laboratory evaluation of samples collected in the field)

The following tests are recommended to be performed onshore in the laboratory because vibration on the platform interferes severely with the method:

(1) Surface tension
(2) Viscosity

Containers for collecting the required samples are included in the test kit.

Tests Not Recommended

The following OOC test procedures were not included in the SRI test kit:

(1) Infrared oil-in-water using the Horiba* and Turner spectrophotometers
(2) Gravimetric oil-in-water using balance at test site
(3) Particle size
(4) Brine composition
(5) Flow rate (site-specific equipment for each platform should be used for these measurements)
(6) Water cut
(7) Boiling range

Selection and Comparison of Oil Analysis Methods

Infrared Method—Three spectroscopic oil-in-water analyzers were compared for field application: the Horiba, Model OCMA-200; the Wilks Miran, Model 1A-FF; and the Turner Spectronic, Model 350. Tests showed (Table 3) that the Miran spectrophotometer provides more reproducible results and is the instrument of choice for the infrared method. This analyzer is powered by 120 VAC and can probably be obtained as a battery-powered model; but it is not explosion-proof.

Gravimetric Method—Table 4 compares the infrared and gravimetric methods for analysis of oil in seawater. For the comparison, we chose to use No. 6 fuel oil because of the unavailability of crude samples with similar properties to the oil from the Alaskan production sites. We assumed that methods developed with No. 6 fuel oil should be applicable to crude oil samples. For a sample of Freon 113 containing a known weight of No. 6 fuel oil, the gravimetric method, which involved evaporation of the Freon and weighing of the residuals, gave 95% recovery of the oil. These results suggest that some volatiles (5%) are lost during evaporation. In extraction experiments, however, the oil recovery by both the infrared (extraction and measurement by the Miran) and gravimetric (extraction, evaporation, and weighing) methods is significantly lower, presumably because of the poor extraction efficiency of Freon 113.

Solvent Extraction Efficiency

As shown in Table 5, CCl_4 is more efficient than Freon 113 in dissolving No. 6 fuel oil suspended in seawater. With Freon 113, small black flakes of residual material remain undissolved.

We also observed that the purity of the Freon used in the extraction process affects the oil analysis results. The absorbence background for Freon TF (an impure grade of Freon 113) was considerably greater than spectral grade Freon 113; a nonlinear calibration curve for No. 6 fuel oil was observed with the impure solvent. Since the nonlinear calibration is less sensitive to small differences in oil content, we suggest that more accurate results could be obtained using the higher-priced Freon 113.

Test Kit Performance

The test kit evaluated and assembled at SRI performed satisfactorily at the two test sites. Only minor modifications to the test procedures were required. Approximately 8 labor-hours are required to conduct one onsite oil-brine characterization.

During this study, it became apparent that the complete field test kit is rather bulky (132.3 lb) for one person to

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Table 2. *Recommended and Modified Procedures for the Field Test Kit*

Test No.	Test	TI Method†	Reason for Test	SRI Recommendation/Modification
1a*	Oil-in-water, infrared	Filtered Freon extract analyzed with the Horiba	Measure total concentration of oil in effluent	Analyze with the Miran 1A-FF*, use Freon 113 rather than Freon TF
1b*	Oil-in-water, gravimetric	Balance in lab	Verify infrared data	No change, but question necessity
2a	Soluble materials, silica gel	Silica gel in Freon extract analyzed with Horiba	May not correspond directly to soluble oil content	Drop test
2b*	Soluble materials, equilibration	Lab with no agitation	Measure water soluble component of oil	Agitate sample and centrifuge to remove oil drops
2c*	Soluble materials, filtration	Filter water, then analyze with the Horiba	Measure concentration of soluble hydrocarbons in water	Filter and analyze with Miran 1A-FF
3	Particle size	Continuous flow microscope assembly	Determine physical characteristics of oil in effluent	Drop test
4*	Surface tension	DuNouy ring tensiometer	Detect surface active agents that may interfere in oil/water separation	Conducted in laboratory
5*	Viscosity	Cannon-Fensk kinematic	Characterize oil	Use Brookfield viscometer
6*	Specific gravity	Hydrometers	Characterize oil	No change
7*	pH	Battery-operated pH meter	Characterize brine	No change
8*	Temperature	Dial thermometer	Characterize brine	No change
9	Brine composition	Assorted methods (lab)	Characterize brine	Drop test
10*	Bacterial culture	Serial dilution	Estimate bacterial population	No change
11	Oil separation	Rise time of oil measured in separatory funnel	Estimate ease of separating the oil and water	Drop test
12*	Suspended solids	Filter holders	Characterize brine	No change
13	Flow rate	Clampitron flowmeter	Measure volume of effluent	Drop test
14	Water cut	Centrifugation	Measure ratio of water to oil in production stream	Drop test
15	Boiling range	GC	Characterize oil	Drop test

*Included in SRI field test kit.
†From Reference 3.

Table 3. *Comparison of Three Oil-in-Water Analyzers*

Feature		Instrument	
	Horiba	Miran	Turner
Weight (kg)	8.9	6.5	7.4
Wavelength (nm)	3400-3500	3400-3500	620 for No. 6 oil 340 for No. 2 oil
Solvent	CCl_4 or Freon	CCl_4 or Freon	$CHCl_3$
ppm oil measured directly on scale	0-100	0-3500	0-4000
Oil analysis (ppm)* 1.	592 ± 12	588 ± 5	656 ± 16
2.	640 ± 12	552 ± 6	676 ± 5
3.	656 ± 10	648 ± 6	664 ± 0
4.	490 ± 40	536 ± 0	582 ± 2
5.	562 ± 10	488 ± 0	478 ± 2
6.	516 ± 10	576 ± 10	526 ± 14
Average deviation	± 16	± 5	± 7

*Oil-in-water samples from six different EPA dispersant effectiveness tests[4] were analyzed on all three instruments. Each test was duplicated, and the average and the deviation are reported.

transport easily. We therefore recommend that the kit be simplified to focus only on the oil-in-water analysis. A field test kit for measuring the oil content of the platform effluent by the infrared method would probably consist of one suitcase (28-lb), the Miran spectrometer (21 lb), and the Freon solvent bottles (40 lb). The onsite analysis time required to conduct the single measurements would also be shortened from about 8 labor-hours (to conduct all the tests) to about 2 labor-hours.

References

1. "Study of Pollution Control Technology for Offshore Oil Drilling and Production Platforms," Exxon Research and Engineering, Linden, New Jersey, EPA Contract No. 68-03-2337 (February 1977).
2. Offshore Operators' Committee Comments on: "Study of Pollution

Table 4. Comparison of the Infrared and Gravimetric Oil Analysis Methods

Infrared Methods			Gravimetric Methods		
No. 6 Oil Added (mg)	*No. 6 Oil Recovered (mg)*	*Recovery %*	*No. 6 Oil Added (mg)*	*No. 6 Oil Recovered (mg)*	*Recovery (%)*
			42⁺	40	95
41	34	82	41	36	87
32	27	85	32	25	78
38	31	80	38	26	68
Average	—	82	—	—	78
Std. Dev.	—	3	—	—	10
% Std. Dev.	—	4	—	—	13

**Oil extracted from 500 ml of seawater with Freon 113 + 3 ml 12M HC1.*
+Oil dissolved directly in Freon 113.

Table 5. Solvent Extraction Efficiency for No. 6 Fuel Oil

*Extractant**	*Oil Added (mg)*	*Oil Recovered (mg)*	*% Recovery*
$CC1_4$	57	54	95
	53	52	98
	62	59	95
	56	54	96
Average	—	—	96
Std. Dev.	—	—	1
% Std. Dev.	—	—	1
Freon 113	43	31	72
	34	29	85
	44	25	57
Average	—	—	71
Std. Dev.	—	—	14
% Std. Dev.	—	—	20
Freon 113†	41	34	83
	32	27	84
	38	31	82
Average	—	—	83
Std. Dev.	—	—	1
% Std. Dev.	—	—	1

**Oil extracted from 500 ml seawater.*
†+3 ml 6M HC1

Control Technology for Offshore Oil Drilling and Production Platforms," EPA Contract No. 68-03-2337 (June 1977).

3. "Field Verification of Pollution Control Rationale for Offshore Oil and Gas Production Platforms," Texas Instruments, Inc. Ecological Services, Dallas, Texas, EPA Contract No. 7-3-002-8 (May 30, 1979).
4. L.T. McCarthy, I. Wilder, and J. S. Dorrler, "Standard EPA Dispersant Effectiveness and Toxicity Tests," EPA-R2-73-201 (May 1973).

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The complete report, entitled "Field Test Kit for Oil-Brine Effluents from Offshore Drilling Platforms," (Order No. PB 82-105 602; Cost: $6.50, subject to change) will be available only from:
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
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