SRI International

FIELD TEST KIT FOR OIL-BRINE EFFLUENTS FROM OFFSHORE DRILLING PLATFORMS

by

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

The objectives of the present research program were (1) to develop and evaluate a field test kit for characterizing oil-brine effluents from offshore drilling platforms and (2) to deliver to EPA the completely assembled kit with detailed operating instructions for conducting each test method.

ABSTRACT

This research program was initiated to evaluate test methods for characterizing oil-brine effluents from offshore oil production platforms and to package and deliver a field test kit for on-site oil-brine analyses. After an initial laboratory evaluation and selection of test methods and equipment, two on-site oil-brine analyses of production water were conducted in Kenai, Alaska--one at the AMACO Dillon Offshore Production Platform, and the other at the Shell MGS Joint Onshore Facility. This report describes the methods developed for the field test site, including detailed procedures for conducting each test method, and the results from the two on-site analyses.

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SECTION 1

INTRODUCTION

Offshore drilling facilities are becoming increasingly numerous as new oil reserves are needed to replace depleted land-based sources. As a result, the possibilities of 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 is routinely pass 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 results 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 evaluating the efficiency of the oil-brine separation process. The Offshore Operators' Committee (OOC) reviewed the Exxon procedures and recommended several modifications.[2] Additional changes have been proposed and verified by field evaluation by Texas Instruments Incorporated.[3]

A summary of the OOC test methods is given in Table 1. Specifically, the work at 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.

3. Evaluate the field test kit at a suitable onshore or offshore oil production facilitiy.

4. Deliver the field test kit to EPA with detailed instructions for performing the tests.

TABLE 1. SUMMARY OF OOC TEST METHODS

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.

SECTION 2

CONCLUSIONS

METHODS REVIEW AND DEVELOPMENT

The OOC-recommended test procedures, a brief description of the test as suggested by the Texas Instruments report[3], and our recommendations and modifications to these tests are summarized in Table 2.

RECOMMENDED TESTS FOR FIELD TEST KITS

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

(1) Oil in water (IR 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 or 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.

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

(1) IR oil-in-water, using the Horiba and Turner spectrophotometers.

(2) Gravimetric oil-in-water, using balance at test site.

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, IR	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 IR 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 & 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.

(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

FIELD RESULTS

The test kit evaluated and assembled at SRI performed satisfactorily at the two test sites. Only minor modifications to the test procedures, as outlined in Section 4, were required. Approximately 8 labor-hours are required to conduct one on-site oil-brine characterization.

SECTION 3

RECOMMENDATIONS

During this study, it became apparent that the complete field test kit is rather bulky (132.3 lb) for one person to transport easily. Therefore, we 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 on-site 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.

SECTION 4

EXPERIMENTAL RESULTS

METHODS REVIEW AND DEVELOPMENT

Total Oil Content

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. The results, shown in Table 3, suggest that the Miran spectrophotometer provides more reproducible results and is the instrument of choice for the infrared method. It is powered by 120 VAC, can probably be obtained as a battery-powered model, but is not explosion proof.

The Miran analyzer has definite advantages over the Horiba instrument and some advantages over the Turner. The Miran's reproducibility, range, and easily cleaned sample cell are similar to the Turner analyzer; it also gives similar extinction coefficients for the same oils. The largest difference in extinction coefficients found on the Miran was 30% between No. 2 fuel oil and light Arabian crude. The Turner instrument uses visible and near UV light and requires different wavelengths for No. 2 and No. 6 fuel oils.

The requirement to adjust the wavelength for different oils could cause errors in the total oil measurements from small variations in the oil composition during a sampling period. For optimum results, all three instruments require calibration with an oil that is similar to the oil being sampled. A critical review of the Horiba[4] recommended that the automatic extractor should not be used. The Miran performs the same measurement as the Horiba and uses the extraction procedure recommended in the review.[4]

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. It seemed reasonable 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 the residuals, gives 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.

TABLE 3. COMPARISON OF THREE OIL-IN-WATER ANALYZERS

INSTRUMENT / FEATURE		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[5] were analyzed on all three instruments. Each test was duplicated, and the average and the deviation are reported.

TABLE 4. COMPARISON OF THE INFRARED AND GRAVIMETRIC METHODS

Infrared Method			Gravimetric Method		
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 seawater with Freon 113 + 3 ml 12M HCl.

+Oil dissolved directly in Freon 113.

TABLE 5. SOLVENT EXTRACTION EFFICIENCY FOR No. 6 OIL

Extractant*	Oil Added (mg)	Oil Recovered (mg)	Percent Recovery
CCl_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 HCl

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 absorbance 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 can be obtained using the higher priced Freon 113.

Soluble Oil

There has been some concern that a water-soluble fraction of the oil might cause an inaccuracy in the oil measurement since the composition and, therefore, the extinction coefficients of dispersed and dissolved oils are expected to be different. A sample of No. 6 fuel oil was shaken vigorously for four days in the presence of 400 ml of synthetic seawater. The aqueous phase was centrifuged to bring any dispersed oil to the surface, and the resultant film of oil was skimmed off the water surface. Microscopic analysis of the water showed that no oil droplets remained. A sample of the aqueous phase was extracted with CCl_4 and analyzed for oil content with the Miran 1A-FF. The results showed that only 3 ppm soluble oil was present. This suggests that the major fractions measured by the oil-in-water analyses are dispersed oil, not dissolved oil.

In a similar test, little change was observed in the apparent oil content of a standard No. 6 oil sample in CCl_4 before and after treatment with SiO_2 gel. Since a similar low level of soluble oil is expected with a crude oil, the OOC-recommended silica gel adsorption task is not necessary.

Particle Size

Particle size distribution of dispersed oil was measured using a photographic method. A sample of oil dispersed in water was placed on a capillary slide. At least three representative areas in the sample were photographed within 15 minutes at a magnification great enough to distinguish the sizes of the smaller particles. Statistical analysis requires more than 100 particles to be counted from each sample; when fewer particles are present, more photographs should be taken.

To calibrate the photographs of the oil droplets, we placed a transparent reticule on the photographs for size determination. The reticule had been calibrated on a picture of a stage micrometer taken at the same magnification as the oil droplets. A log normal distribution best described the data, allowing the median to be found graphically. Using this technique, we

found that the median particle diameter decreased 10% in one hour, probably because the larger particles rise to the surface of the capillary slide and out of focus of the camera. This introduces an uncertainty in the measurement. The simple and portable method we have developed can best be used to document the presence of droplets, but is probably not useful for measuring the absolute size distribution.

FIELD RESULTS

The assembled suitcase portion of the field test kit is shown in Figures 1 and 2. The approximate weight and volume of the entire kit is given in Table 6. The tests, conducted on July 7, 1980, at the Dillon offshore Production Platform, Kenai, Alaska, and on July 8, 1980, at the Shell MGS Joint Onshore Facility, Kenai, Alaska, are outlined in Table 2. 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. A complete listing of the instruments and materials provided in the field test kit is given in Appendix A. The experimental procedures for each test are given in Appendix B.

Oil-in-Water Results

Table 8 summarizes the total oil content of the Dillon and Shell production water effluents using the infrared and gravimetric methods. The results have been corrected for the extraction efficiency of Freon 113 for the Dillon and Shell oils in seawater (Table 9). As shown in Table 8, the oil concentration (ppm, w/w) measured by the infrared method for the Dillon production water is higher than that for the Shell water (47.9 versus 38.2 ppm). The gravimetric results for both samples are appreciably lower than the infrared data, suggesting that oil is lost during the solvent evaporation procedure (Appendix A). Similar low results for the gravimetric method for No. 6 oil have been previously noted (Table 4).

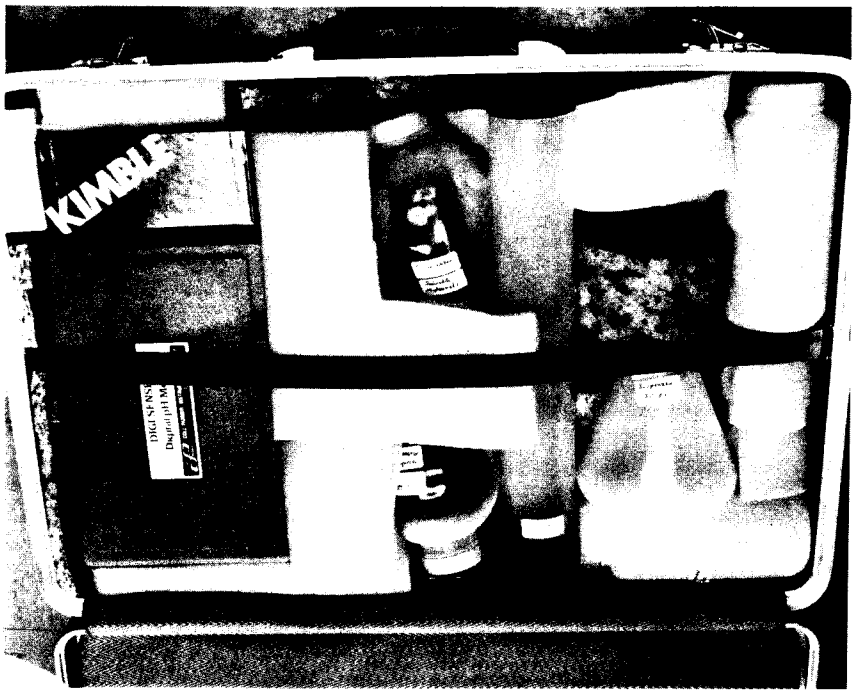
Soluble Materials

Table 10 gives the results for soluble materials. The field method gives comparable results using the infrared and gravimetric techniques, despite a large statistical spread. The laboratory results are somewhat lower, suggesting a loss of material during transportation of the samples to SRI.

Suspended Solids

Suspended solids results are shown in Table 11. For an unexplained reason, the total suspended solids results for the Shell samples are in better agreement than those for the Dillon samples. Other suspended solids results shown in Table 11 are perhaps 10% low because of a filtration problem. Since the original procedure did not call for adequate drying of the filter paper following solvent rinsing, the wet paper adhered to the holder and a small portion was lost for weighing. This difficulty has been corrected in the revised procedure given in Appendix B.

(a) TOP



(b) BOTTOM

FIGURE 1 ASSEMBLED FIELD TEST KIT — SUITCASE NO. 1

TABLE 6. FIELD TEST KIT DIMENSIONS AND WEIGHT

Item	Dimensions (cm)	Weight (kg)
Suitcase no. 1	70 x 50 x 21	12.6
Suitcase no. 2	70 x 50 x 21	11.0
Miran spectrometer and container	29 x 28 x 24	9.5
Freon 113 sample bottles and container	36 x 25 x 29	7.4
Bacterial culture bottles and container	25 x 18 x 12	1.4
Two gallons Freon 113 and container	40 x 25 x 40	18.1
Total Weight		60.0 (132.3 lb)

Physical Properties of Oil and Water

The physical properties (temperature, pH, salinity, density, and viscosity) of the water and oil samples taken at the Dillon and Shell sites are given in Table 7.

TABLE 7. PHYSICAL PROPERTIES OF OIL AND WATER

Test / Site	Production Water			Density (g/cc, 20°C)		Viscosity (cp, 20°C)
	Tem. (°C)	pH	S °/oo*	Water	Oil	Oil
Dillon	48	7.45	30.6	1.015	0.8605	9.3
Shell	34	8.03	25.7	1.012	0.8430	6.5

*Salinity calculated from Standard Methods for the Examination of Water and Wastewater. 14th edition, M. C. Rand, A. E. Greenberg, and M. J. Taras, editors, American Public Health Assoc., Washington, D.C., 1976.

TABLE 8. OIL-IN-WATER RESULTS

Sample	Infrared Method			Gravimetric Method		
	Wt. Oil Obs. (mg)	Wt. Oil Corr. (mg)	ppm (w/w)	Wt. Oil Obs. (mg)	Wt. Oil Corr. (mg)	ppm (w/w)
		*			*	
Dillon No. 1	25.8	27.7	54.6	8.3	8.9	17.5
No. 2	22.7	24.4	48.1	8.8	9.4	18.5
No. 3	17.1	18.4	36.3	9.1	9.8	19.3
No. 4	21.7	23.3	45.9	11.2	12.0	23.6
No. 5	26.7	28.7	56.6	2.6	2.8	5.5
No. 6	21.6	23.2	45.7	9.2	9.9	19.5
Average	22.6	24.3	47.9	8.2	8.8	17.3
Std. Dev.	3.4	3.7	7.3	2.9	3.1	6.2
% Std. Dev.	15.0	15.2	15.2	35.4	35.2	35.8
		+			+	
Shell No. 1	16.1	17.3	34.2	9.5	10.2	20.2
No. 2	19.2	20.6	40.7	16.5	17.7	35.0
No. 3	16.6	17.8	35.2	14.9	16.0	31.6
No. 4	17.2	18.5	36.6	17.4	18.7	37.0
No. 5	18.0	19.3	38.1	11.3	12.1	23.9
No. 6	20.8	22.3	44.1	10.2	11.0	21.7
Average	18.0	19.3	38.2	13.3	14.0	28.2
Std. Dev.	1.8	1.9	3.7	3.4	3.6	7.2
% Std. Dev.	10.0	9.8	9.7	25.6	25.7	25.5

*Corrected for 93.3% extraction efficiency (Table 9).
+Corrected for 93.1% extraction efficiency (Table 9).

TABLE 9. EXTRACTION EFFICIENCY OF FREON 113 FOR DILLON AND SHELL OILS*

Sample	Oil Added (mg)		Oil Recovered (mg)		% Oil Recovered	
	20°C	48°C	20°C	48°C	20°C	48°C
Dillon No. 1	25.9	-	24.1	-	93.1	-
No. 2	25.9	-	23.8	-	91.9	-
No. 3	25.6	-	24.3	-	94.9	-
No. 4	-	25.2	-	20.3	-	80.6
No. 5	-	25.4	-	17.9	-	70.5
No. 6	-	25.6	-	18.8	-	73.4
Average	-	-	-	-	93.3	74.8
Std. Dev.	-	-	-	-	1.5	5.2
% Std. Dev.	-	-	-	-	1.6	7.0
		34°C		34°C		34°C
Shell No. 1	16.4		14.8	-	90.2	-
No. 2	17.4		15.8	-	90.8	-
No. 3	17.2		16.9		98.3	-
No. 4	-	16.3	-	15.5	-	95.1
No. 5	-	16.9	-	13.3	-	78.7
No. 6	-	16.8	-	13.3	-	79.2
Average	-	-	-	-	93.1	84.3
Std. Dev.	-	-	-	-	4.5	9.3
% Std. Dev.	-	-	-	-	4.8	11.0

*Oil extracted from 500 ml seawater.

TABLE 10. SOLUBLE MATERIALS RESULTS

Sample \ Method	Infrared mg/ℓ (ppm)		Gravimetric mg/ℓ (ppm)
	Field	Lab	Field
Dillon No. 1	21.0	9.0	11.6
No. 2	23.8	7.5	35.2
No. 3	16.4	-	11.2
Average	20.4	8.3	19.3
Std. Dev.	3.7	1.1	13.7
% Std. Dev.	18.1	13.3	71.0
Shell No. 1	17.2	5.3	18.6
No. 2	13.2	13.0	11.0
No. 3	12.8	17.8	10.6
Average	14.4	12.0	13.4
Std. Dev.	2.4	6.3	4.5
% Std. Dev.	16.7	52.5	33.6

TABLE 11. SUSPENDED SOLIDS (SS) RESULTS

Sample	Vol (mℓ)	T[1] (mg)	A[2] (mg)	B[3,*] (mg)	C[4,*] (mg)	Total SS (A-T) mg/ℓ	Organic SS* (A-B) mg/ℓ	Acid Soluble SS* (B-C) mg/ℓ	Fixed SS* (C-T) mg/ℓ
Dillon No.1	200	83.3	103.4	102.5	87.8	100.5	4.5	73.5	22.5
No.2	200	83.7	91.9	91.3	87.4	41.0	3.0	19.5	18.5
No.3	200	80.3	86.6	84.6	82.6	31.5	10.0	10.0	11.5
Average	-	-	-	-	-	57.7	5.8	34.3	17.5
Std. Dev.	-	-	-	-	-	37.4	3.7	34.3	5.6
% Std. Dev.	-	-	-	-	-	64.8	63.8	100.0	32.0
Shell No. 1	460	80.5	95.7	-	-	33.0	-	-	-
No. 2	410	80.4	94.6	88.1	83.9	34.6	15.9	10.2	8.5
No. 3	490	82.1	98.0	89.3	85.1	32.4	17.8	8.6	6.1
No. 4	410	81.3	96.1	83.1	78.3	36.1	31.7	11.7	-
Average	-	-	-	-	-	34.0	21.8	10.2	7.3
Std. Dev.	-	-	-	-	-	1.7	8.6	1.6	1.7
% Std. Dev.	-	-	-	-	-	5.0	39.4	15.7	23.3

*Values likely to be ~10% low due to filter paper adherence to holder

1. T = Original weight of filter paper.
2. A = Weight of filter paper following sampling and desiccation.
3. B = Weight of filter paper and solids following $CHCl_3$ wash and desiccation.
4. C = Weight of filter paper and solids following HCl wash and desiccation.

Bacterial Culture

Table 12 gives the bacterial culture test results, expressed in terms of the sulfate-reducing bacteria count. Because of a delay in the air shipment of the samples to SRI, incubation was not initiated within the recommended 24-hour period. As a result, some of the samples arrived at the laboratory indicating an initial positive test. Subcultures were taken of the positive samples and incubated for 1 week at 49°C. Samples, regardless of their condition upon arrival, were also incubated for the prescribed 5-week period at 49°C. The results, however, may not accurately represent the actual microbial content of the production water at the time of sampling, since testing procedures were not initiated within 24 hours.

TABLE 12. BACTERIAL CULTURE RESULTS

Sample	Dilution	Original Condition on Arrival	After Incubation 5 Weeks at 49°C	Subculture*
Dillon No.1	10	+	+	+
	10^2	-	+	
	10^3	-	-	
	10^4	-	-	
	10^5	-	-	
	10^6	-	-	
Bacteria/ml			$10^2 - 10^3$	
Shell No. 1	10	+	+	+
	10^2	-	+	
	10^3	-	-	
	10^4	-	-	
	10^5	-	-	
	10^6	-	-	
Bacteria/ml			$10^2 - 10^3$	
Shell No. 1	10	+	+	+
	10^2	+	+	+
	10^3	+	+	+
Bacteria/ml			ca. 10^3	
Shell No. 3	10	+	+	+
	10^2	+	+	+
	10^3	-	-	
	10^4	-	-	
Bacteria/ml			$10^2 - 10^3$	

* Subcultures were made of any culture that arrived at the lab already indicating a positive result. These subcultures were made after the original culture was incubated for 1 week at 49°C.

+ Positive test, sulfate-reducing bacteria present.

- Negative test, no bacteria present.

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 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. T. S. Yu and W. H. Coleman, "Evaluation of the Horiba Model OCMA-200 Oil Content Analyzer," David W. Taylor Naval Ship Research and Development Center, Report MAT-77-63 (November 1977)

5. L. T. McCarthy, I. Wilder, and J. S. Dorrler, "Standard EPA Dispersant Effectiveness and Toxicity Tests," EPA-R2-73-201, May 1973.

APPENDIX A

INSTRUMENTATION AND MATERIALS PROVIDED IN THE FIELD TEST KIT

2 Separatory funnels, 1 liter, Teflon
4 Erlenmeyer flasks, 125 ml, glass
4 Volumetric flasks, 100 ml, glass
2 Funnels, small, glass
1 Repipet, 10 ml
1 Ring stand, metal
2 Rings, metal
1 Miran spectrophotometer, oil analyzer
1 Graduated cylinder, 1000 ml, plastic
1 Graduated cylinder, 500 ml, plastic
1 Graduated cylinder, 100 ml, plastic
1 Box disposable pipets, glass
1 Package disposable pipet bulbs
1 Buchner funnel
2 Buchner support rings (Filter-vac)
2 Hand vacuum pumps
1 Box filter paper, 7 cm, Whatman No.1
1 Filter flask
12 Glass filters in holders
1 Forceps
1 Wash bottle for distilled water, 500 ml
2 Liters distilled water
1 Portable pH meter
2 pH electrodes
3 Buffer solutions, pH 4, 7, and 10
2 Beakers, 100 ml, polyethylene

2 Beakers, 500 ml, polyethylene

1 Mercury thermometer, -20 to +100°C

1 Dial thermometer, 0 to 100°C

25 Disposable sterile syringes, 1 cc

1 Insulated sample box

24 Sample bottles for bacterial culture medium, 10 ml

1 Hydrometer set

6 Square glass bottles, 250 ml

24 Glass bottles with Teflon-lined caps, 2 oz

1 Pair gloves, neoprene

1 Box large Kimwipes

1 Box small Kimwipes

100-g Alconox cleaner

500-ml Hand cleaner

1 Sponge

1 Pack Kimtowels

2 Bottle brushes

1 Roll electrical tape

1 Box labels

APPENDIX B

LABORATORY AND FIELD PROCEDURES

OIL-IN-WATER

Field Equipment

Graduated cylinders,500 ml, 100 ml
Separatory funnel, 1 liter
Freon 113
Ring stand
Erlenmeyer flask, 250 ml
Volumetric flask, 100 ml
Miran spectrophotometer
Sample bottle with Teflon-lined cap
Disposable pipets

Field Procedure

(1) Purge sample port. Fill 500-ml graduated cylinder from sample port.
(2) Transfer sample directly to a 1-liter Teflon separatory funnel, rinse, graduate with 25 ml of Freon 113. Add Freon rinse to separatory funnel along with the sample.
(3) Swirl separatory funnel about 5 times and invert 10 times to extract the oil from the brine. Place separatory funnel upright in the ring stand and allow layers to separate completely.
(4) Drain lower Freon layer into a 250-ml Erlenmeyer flask, being careful not to include any brine. Repeat extraction two more times with 25-ml aliquots of Freon.
(5) Transfer solvent sample from Erlenmeyer to a 100-ml volumetric flask. Rinse the Erlenmeyer with more Freon and add it to the volumetric flask; then add enough Freon to fill the flask to the mark.
(6) Zero spectrophotometer using Freon from the same batch used for the extraction of the oil. Place the cell in the Miran spectrophotometer and zero the reading at all sensitivities. Zeroing should be done every time the spectrophotometer is turned on and once every few hours, if used continuously.

(7) Use a disposable pipet to transfer the Freon extract to a spectral cell and place the cell in the Miran. Adjust the range to obtain the highest reading without going off scale. Record this meter reading and the setting of the spectrophotometer.

(8) Save sample for lab analysis. Rinse a sample bottle with Freon. Transfer the sample in the cuvette and the volumetric flask into the sample bottle. Rinse both the cuvette and volumetric with additional Freon and add to sample.
(9) Seal the bottle and label it with the sample no., where and when the sample was taken, and who performed the analysis.

Laboratory Procedure (IR Method)

(1) To calibrate the spectrophotometer, obtain a sample of the crude oil produced on the platform of interest. Draw 200-µl of crude oil into a syringe and weigh it on an analytical balance to the nearest 0.001 g; record the weight. Empty the contents of the syringe into a 500-ml volumetric and reweigh the empty syringe. Record this weight below the previous weight and subtract to obtain the actual weight of the oil. Fill the volumetric to the mark with Freon 113. Pipet 10-, 25-, 50-, and 75-ml aliquots into four 100-ml volumetrics and bring them to the mark with Freon.

(2) Measure the absorbance of each of the solutions by the same method cited in the field procedure. Plot these data to determine the curve for oil concentration (mg/cc) versus absorbance.

Correction Factor for Extraction Efficiency

(1) Prepare 2 liters of synthetic brine of the same salinity and pH reported on the platform by dissolving NaCl in distilled water (see specific gravity and pH sections). Adjust pH with NaOH or HCl.
(2) Place 500 ml of brine into four separatory funnels; then use the same procedure used in the spectrophotometer calibration section to weigh a known amount of oil. This amount should be the average amount of oil that was found on the platform. Record the absorbance, setting, and the weight of the oil added to each separatory funnel for calculation. Extract with Freon as described in the field procedure.

Laboratory Procedure (Gravimetric Method)

(1) Pour a Freon sample into a tared 250-ml Erlenmeyer flask. Rinse the sample bottle with 10 ml of Freon and add this to the flask. Peel off the label and tape it into the lab book.
(2) Place the flask in a thermostated water bath at 50°C and allow almost all of the Freon to evaporate. Remove the flask from the bath and run clean N_2 gas over the surface at room temperature until no more Freon is visible. Place in a vacuum desiccator overnight to remove any water present. Weigh the flask with the residue and record the weight.

Calculations

(1) Oil-in-Water (IR Method)

$$\text{ppm (mg/ℓ)} = \frac{\text{mg oil in Freon x ml Freon sample}}{\text{original brine sample volume (ℓ)}}$$

(2) Oil-in-Water (Gravimetric Method)

$$\text{ppm (mg/ℓ)} = \frac{\text{mg oil residue}}{\text{original brine sample volume (ℓ)}}$$

(3) Extraction Efficiency

$$\text{\% Oil Recovery} = \frac{\text{mg/cc oil in Freon x mℓ Freon sample}}{\text{mg oil added}} \times 100$$

SOLUBLE MATERIALS [(FILTRATION AND EQUILIBRATION)]

Field Equipment

Buchner funnel
Filter papers, 7 cm
vacuum filtration apparatus
Graduated cylinder, 1 liter
Separatory funnel, 1 liter
Freon 113
Ring stand
Erlenmeyer flask, 250 ml
Volumetric flask, 100 ml
Miran spectrophotometer
Sample bottles with Teflon-lined caps

Field Procedure

(1) Assemble vacuum filtration apparatus. Place filter paper in a Buchner funnel and wet it with distilled water.
(2) Purge sample port. Fill 1-liter graduated cylinder with brine sample.
(3) Fill Buchner funnel with brine; filter and discard filtrate. Filter 500 ml of sample. Extract this filtrate sample with Freon 113 as described in the oil-in-water field procedure and measure the absorbance accordingly.
(4) Transfer sample to Teflon-capped bottle. Label with sample number, date, location, time, volume, and person who performed test. Then transport samples to the lab for gravimetric analysis.

Laboratory Procedure

(1) Place 400 ml of synthetic brine (use the same salinity and pH described in the lab procedure of the oil-in-water test) in a 500-ml stoppered Erlenmeyer flask.
(2) Syringe 5 ml of the crude oil from the platform of interest into each of the brine solutions. Shake the flasks vigorously for 4 days.
(3) Transfer to a separatory funnel and drain the aqueous phase into centrifuge tubes. Set up a vacuum trap with a disposable pipet at the end and siphon off any oil film present. Centrifuge this solution at 3.8×10^3 g for 1 hr.
(4) Remove the oil film again. Measure 200 ml of the brine in a volumetric and transfer it to a separatory funnel. Rinse the volumetric flask with Freon and add to separatory funnel. Extract the sample with three 10-ml aliquots of Freon and fill to the mark of a 50-ml volumetric flask. Measure and record the absorbance from the spectrophotometer.

Calculations

(1) Soluble materials (IR field method)

$$\text{ppm (mg/}\ell\text{)} = \frac{\text{mg/cc oil in Freon x sample volume (m}\ell\text{)}}{\text{original brine sample volume (}\ell\text{)}}$$

(2) Soluble materials (Lab Method)

$$\text{ppm (mg/}\ell\text{)} = \frac{\text{mg/cc oil in Freon x sample volume (m}\ell\text{)}}{\text{original brine sample volume (}\ell\text{)}}$$

TEMPERATURE AND pH

Field Equipment

pH meter
Buffer solutions (pH 4, 7, 10)
Dial thermometer
Mercury thermometer
Graduated cylinder, 1 liter

Field Procedure

(1) Calibrate the pH meter immediately before each use. Immerse the combination electrode into pH 7 buffer. Adjust temperature knob to the temperature of the sample. Adjust the calibration knob to pH 7 reading. Remove electrode, rinse with deionized water, and wipe clean. See operator's manual for additional

information regarding pH meter.

(2) Calibrate the dial thermometer against a mercury thermometer once a day. Record any difference in the readings.

(3) Purge sample port. Collect 1 liter of sample in a graduated cylinder and immediately insert the dial thermometer. Wait 1 min until the thermometer has equilibrated and read the temperature. NOTE - If the sample site has a temperature well, place the thermometer directly into the port, wait 1 min, and read the temperature.

(4) Immerse combination electrode in sample and agitate gently for 30 sec. Read pH after steady state has been achieved. Remove electrode, rinse with deionized or clean tap water, and wipe clean. If the pH is > 10, calibrate using the pH 10 buffer.

SPECIFIC GRAVITY (OIL AND WATER), SALINITY

Field Equipment

Graduated Cylinder, 1 liter
Thermometer, mercury, -20 to +100°C
Hydrometer Set
3 Square sample bottles, 250 ml
2 polyethylene bottles, 1 liter

Field Procedure

(1) Fill square sample bottles with crude oil to be used in laboratory analysis. Also, fill polyethylene bottles with production water for laboratory determination of salinity. Label and seal all samples for transport.

(2) Purge sample port. Fill a 1-liter graduated cylinder from sample port without splashing, to avoid the formation of air bubbles.

(3) Insert a thermometer into the sample and allow time for equilibration. Record the temperature after gently stirring the sample with the thermometer.

(4) Lower the hydrometer into the sample. Take care to avoid wetting the stem above the level to which it will be immersed in the liquid. Depress the hydrometer about two scale divisions into the liquid, and with a slight spin, release it. When the hydrometer has come to rest, floating freely away from the walls of the cylinder, estimate the scale reading to the nearest 0.0001 sp.gr.

(5) Immediately after observing the hydrometer scale value, stir the sample with the thermometer and record the temperature. Should this temperature differ from the previous reading by more than 0.5 °C, repeat the measurement until the temperature is stable within 0.5°C.

(6) With an opaque liquid, take a reading by observing, with the eye slightly above the plane of the surface of the liquid, the point on the hydrometer scale to which the sample rises. Correct this

reading based on the meniscus calibration for the particular hydrometer being used.

Laboratory Procedure

(1) Follow the field procedure for measuring specific gravity, and determine the density of the production water obtained in the field.
(2) Convert findings to salinity (^{o}/oo) from the tables included in No. 209B "Hydrometric Method for Salinity Determination," in Standard Methods for the Examination of Water and Wastewater, 14th Edition (American Public Health Association, Washington, D.C., 1976).

VISCOSITY

Laboratory Equipment

Brookfield Model LVF Spindle Viscometer
U.S. Bureau of Standards calibrated oils for viscosity testing
Beaker, 600 ml
Thermometer, 0 to 110°C
Oil Sample from platform of interest

Laboratory Procedure

(1) Follow the operating instructions for the viscometer.
(2) Calibrate the viscometer with a certified standard having a specific gravity close to that of the oil in question.
(3) The temperature of the test oil should be controlled to within ± 0.02°C.
(4) Report results in units of centipoise (cps).

SUSPENDED SOLIDS

Field Equipment

Preweighed glass fiber filters/holders
Vacuum filtration apparatus
Forceps
Distilled water
Graduated cylinder, 1 liter

Field Preparation

(1) Desiccate filters overnight before field expedition.
(2) Weigh filters, using an analytical balance, and then place each filter in a holder. Label the holders numerically, recording the weight of each respective filter.

Field Procedure

(1) Purge sample port and fill a 1-liter graduated cylinder with brine.
(2) Assemble the vacuum filtration apparatus. Place a previously weighed glass filter in a Buchner funnel with forceps and wet it with distilled water.
(3) Apply a vacuum and filter the brine until the paper begins to clog. If there are few solids present, use the full liter. Record the volume of brine filtered.
(4) Rinse the filter with 100 ml of distilled water; then draw air through to partially dry it. Replace filter in its holder with forceps; close the lid.
(5) Record the date on the holder and the conditions under which the sample was taken. At the end of the sampling period, all the filter holders should be firmly taped together so that they do not open during transport back to the lab.

Laboratory Procedure

(1) Remove the tops of the filter holders and dry the filters in a vacuum desiccator overnight; then weigh the filter and record the weight (A).
(2) Assemble the vacuum filtration apparatus. Place the filter in the buchner funnel right side up, and wash with three 25-ml aliquots of $CHCl_3$. Dry the filters with air; then return to the desiccator overnight. IMPORTANT - Do not place filters into the plastic holders to desiccate because the $CHCl_3$ will cause the filter to adhere to the holder. Remove the following day, reweigh, and record the weight (B).
(3) Wash the filter with 100 ml 6N HCl and vacuum dry. Desiccate the filter overnight. Weigh the filter for a final time and record this weight (C).

Calculations

Using the original weight of the filter as T, calculate the following:

Total suspended solids	= A - T
Organic suspended solids	= A - B
Acid-soluble suspended solids	= B - C
Fixed suspended solids	= C - T

Convert findings to parts per million (mg/ℓ):

$$\text{ppm (mg/ℓ)} = \frac{\text{weight (mg)}}{\text{total volume filtered (ℓ)}}$$

BACTERIAL CULTURE: SULFATE-REDUCING BACTERIA

Field Equipment

Serum bottles containing culture medium, 10 ml
Disposable, presterilized syringes, 1 ml
Sterile sample bottle
Insulated sample box.

Field Preparation

(1) Before expedition, prepare the following medium by dissolving the ingredients with gentle heating. Adjust the pH to 7.3 with NaOH. If excessive precipitation occurs, the medium should be discarded.

Sodium lactate, USP,	4.0	ml
Yeast extract	1.0	g
Ascorbic acid	0.1	g
$MgSO_4 \cdot 7H_2O$	0.2	g
K_2HPO_4 (anhydrous)	0.01	g
$Fe(SO_4)_2(NH_4)_2 \cdot 6H_2O$	0.2	g
NaCl	10.0	g
Distilled water	1,000.0	ml

(2) Add reduced iron powder, reagent grade, to the serum bottle and fill with 9 ml of hot broth. Flush the bottles with N_2 gas. Use butyl-type rubber to stopper them; then cap with disposable metallic covers. Sterilize the bottles and contents at 15 psi steam pressure for 15 min.

Field Procedure

(1) Purge sample port.
(2) Use sterile bottle to collect sample. Record time, date, temperature, and water appearance at this time.
(3) All work should be done in duplicate. Using a sterile, disposable syringe, transfer 1 ml of sample to a serum bottle containing the culture medium. Agitate the bottle to mix the inoculum; then using a new syringe, aseptically transfer 1 ml from this bottle to a second one and mix as before. Continue this serial transfer until a dilution of 1 to 1,000,000 is reached (6 bottles).
(4) Place the inoculated bottles in the insulated sample box for transport to the laboratory. Note any bottles that turn black within 2 hours. These should not be considered positive since this probably is due to the presence of sulfide ion in the sample

Subcultures of these false positive samples may be made after 1 week.

Laboratory Procedure

(1) Incubate all bottles at the temperature of the water at the time of sampling, ±5°C, for a minimum of 4 weeks.
(2) Examine the bottles on the third day and at the end of each week for the appearance of sulfate-reducing bacteria, indicated by intense black color. After 1 week, make any necessary subcultures (See Field Procedure, Step 4).

Calculations

(1) Report the data as the highest dilution indicating growth, as compared with the lowest dilution showing no growth. The data are reported as a range in numbers (i.e., 100-1,000 sulfate-reducing bacteria per ml).
(2) The maximuum time between sampling and examination should not exceed 24 hr. If an examination cannot be initiated within this period, include the following statement in the report: "These results do not necessarily represent the actual microbial content of the water at the time of sampling."

Reference

American Petroleum Institute, API Recommended Practice for Biological Analysis of Subsurface Injection Water (American Petroleum Institute, Dallas, Texas, 1975), p. 7.