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Final Report

**LABORATORY TESTING TO DETERMINE DISPERSION PREDICTABILITY
OF THE BAFFLED FLASK TEST (BFT) AND SWIRLING FLASK TEST (SFT)**

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Abstract

In the last few years, dispersants have been widely used as the primary response measure for marine oil spills around the world. Until recently, the U.S. EPA protocol for testing the effectiveness of dispersants in the laboratory was the Swirling Flask Test (SFT), which was found to give widely varying results in the hand of different testing laboratories. As a result, U.S. EPA developed an improved laboratory dispersant testing protocol, called the Baffled Flask Test (BFT). This study tries to evaluate how the dispersant predictability of the BFT compares with that of the SFT. Tests were conducted to determine the effectiveness of two commercially available dispersants, C9500 and SD25 on IFO 180 and IFO 380 oils using the SFT and the BFT.

Introduction

Rapid increase in the demand for petroleum has resulted in a greater potential for oil spills resulting from transportation and consumption of these products. Marine oil spills can have disastrous consequences on the local environment. Among the different cleanup methods available, use of dispersants is the most effective and commonly used. Evidence from spills treated with dispersants show that dispersion of oil can reduce overall environmental impacts by reducing damage at the sea surface and shore. At the same time dispersant use on a spill also reduces intrusiveness, duration, and cost of the cleanup.

Dispersants are mainly mixtures of surfactants and other chemicals, and when applied to the oil slick, remove the oil from the surface and disperse it into the water column (Chandrasekar, 2004). Dispersant effectiveness is a measure of the amount of oil that has been dispersed into the water column compared to the amount that remains on the surface. There are numerous factors that influence the effectiveness of the dispersants such as amount of dispersant added, temperature, type of surfactants, weathering of the oil, mixing energy, salinity and so on. The amount of dispersant added is the most important factor influencing dispersion. In most cases, dispersant effectiveness is directly proportional to the amount of dispersant added. The mixing energy provided by the sea also determines how much dispersion takes place. A rough sea imparts a lot of energy to the mixing of the oil and the dispersant and hence results in good dispersion. The physical and chemical properties of the crude oil also affect its ability to disperse. Oil undergoes weathering when it is spilled; resulting in an increase in its viscosity and the higher viscosity in turn limits the effectiveness of dispersants. Lower water temperature also tends to have a similar effect on the oil, the energy requirement for the mixing of the oil and the dispersant increases to account for the increase in the viscosity. A wide variety of research, both lab and field scale is currently focused on methods to optimize the effectiveness of dispersants.

The BFT is being proposed by EPA as the replacement protocol for listing oil spill remediation products on the National Contingency Plan (NCP) Product Schedule. The reason is that research conducted in 2000-2002 demonstrated that the SFT was

inadequate as a protocol for testing dispersant effectiveness due to its poor reproducibility and repeatability (Sorial *et al.*, 2004; Sorial *et al.*, 2004; Venosa *et al.*, 2002). The primary reasons for the lack of reproducibility were the inadequate mixing regime within the swirling flask and the substantial human error associated with the conduct of the test. In a related subsequent study, Kaku *et al.* (2004) measured the turbulence in the swirling and the baffled flasks at two different mixing speeds using a hot wire anemometer and found that the energy dissipation rate in the BF was more than 2 orders of magnitude greater than that in the SF. This mixing energy was shown to be more in line with published measurements of sea states conducive to good dispersion (Delvigne and Sweeney, 1988). This study compares the dispersant effectiveness of the BFT and the SFT. The two commercial dispersants tested on the two IFO oils, IFO 180 and IFO 380, were C9500 and SD25. The SFT experiments were carried out at 16 °C at a DOR of 1:10 and at a mixing speed of 150 rpm. The BFT experiments were carried out at two different DORs, 1:25 and 1:50, and at a mixing speed of 200 rpm at a temperature of 16 °C.

Materials and methods

Materials

Two different flasks were used in the experiments:

1. The standard EPA SFT flask (U.S. EPA 1996), a 125 mL Erlenmeyer flask with a glass side spout extending from the bottom of the vessel upward to the neck region (spout flask), and

2. Modified 150 mL glass baffled trypsinizing flasks with screw caps at the top and teflon stopcocks placed near the bottom were used in all the experiments (see Figure 1).



Figure 1. Baffled Flask Test Apparatus

An orbital shaker (Lab-Line Instruments Inc, Melrose Park, IL) with a variable speed control unit (40-400 rpm) and an orbital diameter of 0.75 inches (2 cm) was used in order to provide turbulence to solutions in test flasks. The shaker has a control speed dial

to provide an rpm reading on a meter within the instrument. The accuracy is within $\pm 10\%$. A Brinkmann Eppendorf repeater plus pipettor (Fisher Scientific, Pittsburgh, PA) capable of dispensing 4 μL of dispersant and 100 μL of oil with an accuracy of 0.3% and a precision of 0.25% was used with 100 μL and 5mL syringe tip attachments. Glassware consisting of graduated cylinders, 125 mL separatory funnels with Teflon stopcocks, pipettes, 50 mL crimp style amber glass vials and 50, 100 and 1000 μL gas-tight syringes were also used.

Analytical Instruments

A UVmini-1240 UV-VIS Spectrophotometer (UV-VIS spec) (Shimadzu Scientific Instruments, Inc, Wood Dale, IL) capable of measuring absorbance at 340, 370 and 400 nm was used in all the experiments to measure the dispersed oil concentration after extraction.

Reagents

The synthetic sea water “Instant Ocean” (Aquarium Systems, Mentor, OH) was used for all the experiments at a concentration (salinity) of 34 ppt, based on an ion composition shown in table 1. Two types of oil samples provided by US EPA- IFO 180 and IFO380 were used in the study, with characteristics as shown in table 2. The dispersants used for testing of IFO oils were C9500 and SD25.

Table 1. Major Ion Composition of “Instant Ocean” Synthetic Sea Salt

Major Ion	% Total Weight	Ionic Concentration at 34 ppt salinity, mg/L
Chloride	47.5	18,700
Sodium	26.3	10,400
Sulfate	6.6	2,600
Magnesium	3.2	1,200
Calcium	1.0	400
Potassium	1.0	400
Bicarbonate	0.5	200
Boron	0.015	6
Strontium	0.001	8
Solids Total	86.1	34,000
Water	13.9	
Total	100.0	

Table 2. Test Oil Characteristics

Analyte	IFO 180	IFO 380
Specific Gravity at 15°C	0.983 ²	0.990 ²
API Gravity	12.5° ²	11.5° ²
Sulfur	2 wgt.% ¹	3-4 wgt% ³
Nitrogen	---	---
Vanadium	85 mg/L ¹	100-600 mg/L ³
Nickel	---	---
Pour Point	40-60 ° F ²	40-60 ° F ²
Viscosity at 40°C	170 cST ¹ (at 50 °C)	380 cST ³ (at 50 °C)
Viscosity at 100°C	20 cST ¹	35 cST ⁴

Source :

1. http://www.emo.ie/bunkering/product_specs/Emo-PS-IFO-180.pdf
2. http://www.amsa.gov.au/Marine_Environment_Protection/National_Plan/General_Information/Dispersants_Information/Oil-Sea_Temperature_Dispersability_Matrix.asp
3. <http://www.emis.platts.com/thezone/guides/platts/oil/productspecs.html>
4. <http://www.socp.org/projects/completedproj/BunkerFuelOil/images/sample78.doc>

Methods

Oil standard procedure

For the EPA SFT, oil standards or oil–dispersant standards were prepared according to the published method (U.S. EPA 1996). For the BFT, standard solutions of oil for calibrating the UV-VIS spec were prepared with the specific reference oils and dispersant used for a particular set of experimental test runs. For control treatments with no dispersant, i.e, oil control experiments, only oil was used to make the standard solution. Initially, oil alone stock standard was prepared. The density of 2 mL of the specific reference oil with 18 mL DCM added was measured by using a 1 mL gas tight syringe and the concentration of the oil solution was then determined. Specific volumes of 11, 20, 50, 75, 100, 125 μL of IFO 180-DCM stock or the IFO 380-DCM stock were added to 30 mL of synthetic sea water in a separatory funnel and extracted thrice with 5 mL of DCM. The final DCM volume for the combined extracts was adjusted to 20 mL with DCM. The extracts were transferred to a 20 mL crimp style glass vial with a teflon/aluminum seal, mixed by inverting many times and stored in a refrigerator at 4 ± 2 $^{\circ}\text{C}$ until time of analysis. For oil plus dispersant stock standard, to 2 mL specific reference oil, 80 μL of the dispersant (to make a ratio of dispersant:oil = 1:25) was added followed by 18 mL DCM and the density measured using a 1 mL gas tight syringe. For a DOR of 1:50, 40 μL of the dispersant was added to 2 mL of the oil following the same procedure. Based on the amount of oil and dispersant added, and the density measured, the concentration of the stock solution was calculated.

Dispersant effectiveness procedure

All experimental samples were conducted in a temperature controlled room at the desired temperature (16 ± 1 °C). For each sample, four replicates were prepared.

For the **EPA SFT**, the dispersant and oil were premixed in a volume ratio of 1:10. One volume of the dispersant was added to ten volumes of oil in a glass vessel and the vessel was then crimped and mixed vigorously. The premix solution was prepared on the same day of running the dispersant test. A 100 mL aliquot of the oil–dispersant mixture was then dispensed, using an Eppendorf repeater positive displacement pipetter equipped with a 5 mL syringe tip attachment, onto the surface of 120 mL artificial seawater in the spout flask. The flask was then placed on the orbital shaker and mixed for 20 min at a rotation speed of 200 rpm. At the end of the shaking period, the flask was removed from the shaker and allowed to remain stationary for 10 min on the bench top. At the conclusion of the settling time, the first 2 mL of sample from the spout was discarded, and then 30 mL of sample was collected in a 50 mL measuring cylinder. The 30 mL sample was then transferred to a 125 mL separatory funnel and extracted three times with fresh 5 mL DCM. The extract was then adjusted to a final volume of 20 mL and transferred to a 50 mL crimp style glass vial with an aluminum/ Teflon seal. The vials were stored at 5°C until the time of analysis.

For the **BFT**, 120 mL of synthetic sea water equilibrated at the desired temperature was added to the test flask (Fig. 1), followed by the sequential addition of oil and finally the dispersant. 100 µL of oil was dispensed directly onto the surface of the

synthetic sea water using an Eppendorf repeater pipettor with a 5 mL syringe tip attachment. The dispersant was then dispensed onto the center of the oil slick by using a 100 μ L syringe tip attachment that was set to dispense 4 μ L, giving a ratio of dispersant-to-oil ratio (DOR) of 1:25. For DORs other than 1:25, the amount of dispersant added was varied keeping the amount of oil added fixed. To get a DOR of 1:50, 2 μ L of dispersant was used. The flask was placed on an orbital shaker and mixed for 10 minutes at the desired rotation speed of 200 rpm, at the end of which it was removed from the shaker and allowed to remain stationary on the bench top for another 10 minutes. At the end of the settling time, the first 2 mL of sample was drained from the stopcock and discarded, and then 30 mL of sample was collected in a 50 mL measuring cylinder. The 30 mL sample was then transferred to a 125 mL separatory funnel and extracted three times with fresh 5 mL DCM. The extract was then adjusted to a final volume of 20 mL and transferred to a 20 mL crimp style glass vial with a Teflon/aluminum seal. These vials were stored at 4 ± 2 °C until the time of analysis (maximum of 5 days).

The dispersant effectiveness is defined as the concentration of the dispersed oil in water (which is determined through extraction by DCM as stated above) divided by the total concentration of oil, i.e., based on the total volume of oil added.

Sample analysis

The same procedure was followed for the analysis of both SFT and BFT samples. The experimental sample extracts and the standard solutions prepared were removed from the refrigerator and allowed to equilibrate at the laboratory temperature. First, a blank solution (DCM) was introduced. Then the standard solutions were introduced in the

order of increasing concentration and the absorbance values were noted at wavelengths of 340, 370 and 400 nm. After this, the experimental samples were introduced. For samples that exceeded the highest calibration standard point, dilution was done. The sequence of analyses is thus: (1) solvent blank; (2) six calibration standards for the specific test oil plus dispersant and (3) experimental samples.

Calculation procedure

The area under the absorbance vs wavelength curve for the experimental samples between wavelengths 340 and 400 nm was calculated by using the trapezoidal rule according to the following equation:

$$Area = \frac{(Abs_{340} + Abs_{370}) * 30}{2} + \frac{(Abs_{370} + Abs_{400}) * 30}{2} \quad (1)$$

The dispersant performance (i.e, percent of oil dispersed, or Effectiveness) based on the ratio of oil dispersed in the test system to the total oil added to the system was determined by:

$$Eff \% = \frac{\text{Total oil Dispersed}}{\rho_{oil} * V_{oil}} * 100 \quad (2)$$

where:

Δ_{oil} = density of the specific test oil, g/L

V_{oil} = Volume (L) of oil added to the test flask ($100 \mu\text{L} = 10^{-4} \text{L}$)

$$\text{Total oil dispersed, g} = \text{Mass of oil} * \left(\frac{V_{tw}}{V_{ew}} \right) \quad (3)$$

where

V_{tw} = total water volume in the testing flask (120 mL),

V_{ew} = volume of water extracted for dispersed oil content (30 mL).

$$\text{Mass of oil, g} = \text{Concentration of oil} * V_{DCM} \quad (4)$$

where

$$\text{Concentration of oil, g/l} = \left(\frac{\text{Area as determined by equation 1}}{\text{slope of calibration curve}} \right) \quad (5)$$

where, V_{DCM} = the final volume of the DCM-extract of water sample (0.020 L).

The data was entered into a spreadsheet and all the necessary calculations were performed. The data has been attached in the form of tables in appendix 1.

Results and Discussion

Table 1 and 2 show the results obtained for the SFT tests. It can be seen that with the SFT, the dispersant effectiveness achieved with the dispersant C9500 was very low for both oils. For both IFO 180 and IFO 380, the dispersion of oil control was close to zero. The dispersion effectiveness with the dispersant C9500 was less than 10%. Based on these poor results, no further tests were conducted with the SFT for these oils.

Table 1. SFT - Dispersant Effectiveness Test (Oil : IFO 180)

Dispersant	DOR	% Effectiveness of the replicate samples				Average Effectiveness	Coeff. of variation
		R1	R2	R3	R4		
Control	-	0.05	0.05	0.06	0.06	0.05	17.593
C9500	1:10	6.15	7.66	7.36	7.16	7.08	9.235

Table 2. SFT - Dispersant Effectiveness Test (Oil : IFO 380)

Dispersant	DOR	% Effectiveness of the replicate samples				Average Effectiveness	Coeff. of variation
		R1	R2	R3	R4		
Control	-	0.05	0.05	0.06	0.04	0.05	9.540
C9500	1:10	4.38	4.66	5.21	4.26	4.62	9.168

The results for the BFT tests run on the two oils, IFO 180 and IFO 380, are shown in Tables 3 and 4 and have been plotted in Figure 2.

Table 3. BFT - Dispersant Effectiveness Test (Oil : IFO 180)

Dispersant	DOR	% Effectiveness of the replicate samples				Average Effectiveness	Coeff. of variation
		R1	R2	R3	R4		
Control	-	2.79	2.64	2.44	2.75	2.66	5.914
C9500	1:25	77.43	74.57	75.64	78.69	76.58	2.395
	1:50	69.86	69.81	76.52	73.77	72.49	4.508
SD25	1:25	78.21	80.14	80.88	78.60	79.46	1.589

Table 4. BFT - Dispersant Effectiveness Test (Oil : IFO 380)

Dispersant	DOR	% Effectiveness of the replicate samples				Average Effectiveness	Coeff. of variation
		R1	R2	R3	R4		
Control	-	4.04	3.76	3.55	4.05	3.85	6.316
C9500	1:25	65.65	63.70	67.44	62.44	64.81	3.392
	1:50	39.35	37.53	42.77	42.35	40.50	6.175
SD25	1:25	50.61	60.65	61.81	52.99	56.52	9.820

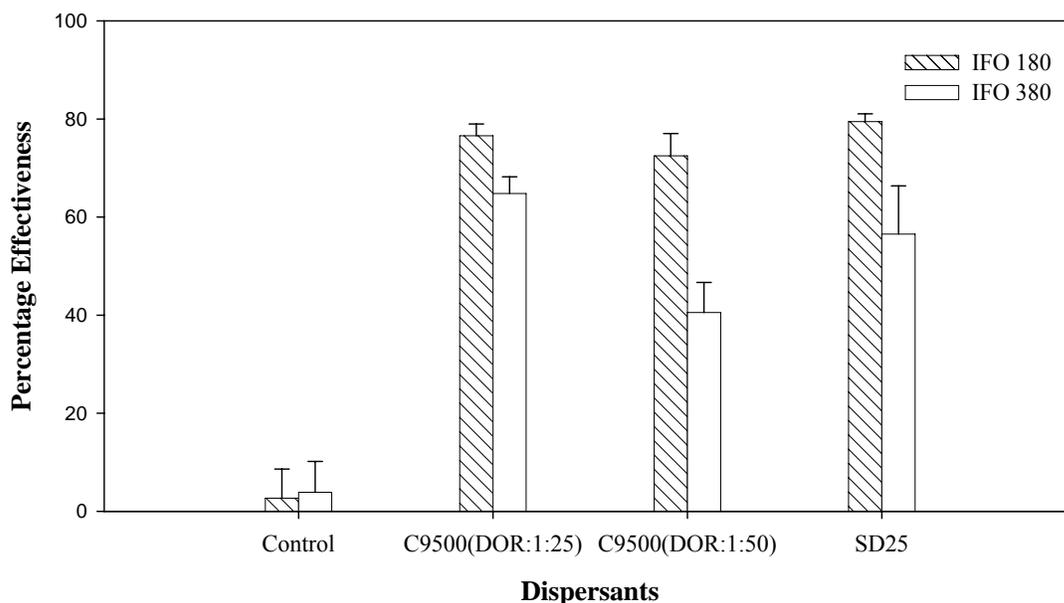


Figure 2. Dispersant Effectiveness for IFO 180 and IFO 380 at 16±1°C

It can be observed that the overall dispersant effectiveness is significantly higher for IFO 180 than IFO 380 for both dispersants. This could be attributed to the higher viscosity of IFO 380 (see Table 2). For both oils, very little dispersion was observed when the tests were run without any dispersant. For IFO 180, the performance of the two dispersants at the same DOR is almost the same whereas for IFO 380, the effectiveness of C9500 is slightly higher than that achieved with SD25. In order to study the effect of DOR on dispersant effectiveness, the tests with C9500 were run at two different DORs, namely 1:25 and 1:50. As expected, the dispersant effectiveness achieved at the higher DOR is higher than that at the lower DOR. This effect was observed to be more pronounced for IFO 380.

Conclusion

The SFT gave very poor results with dispersant effectiveness being less than 10% at a dispersant to oil ratio (DOR) of 1:10, mixing speed of 150 rpm and at a temperature of 16 ± 1 °C. Further testing with SFT was deemed fruitless.

For the BFT, the dispersant effectiveness achieved was considerably higher for both dispersants and for both IFO 180 and IFO 380 oils. The increase in DOR also resulted in a significant increase in dispersant effectiveness and was more pronounced for IFO 380. Overall, IFO 380, with its higher viscosity was less susceptible to dispersion when compared to IFO 180. However, further evaluations looking into the effect of different variables like DOR, mixing speed and temperature on dispersant effectiveness need to be conducted.

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